pollutant concentration monitor and an O_2 or CO_2 diluent gas monitor), for measuring and recording SO_2emission rate (in lb/mmBtu) at the outlet to the emission controls and who uses the applicable procedures, methods, and equations such as those in EPA Method 19 in appendix A to 40 CFR part 60 to estimate the SO_2 emissions removal efficiency of the emission controls, may use the following equations to estimate daily CO_2 mass emissions from sorbent (in tons).

$$SE_{CO_2} = F_u \frac{W_{SO_2}}{2000} \frac{MW_{CO_2}}{MW_{SO_2}}$$

(Eq. G–6)

where,

SE_{CO2}=CO_2 emitted from sorbent, tons/day.

MW_{CO2}=Molecular weight of carbon dioxide (44).

MW_{SO2}=Molecular weight of sulfur dioxide (64).

W_{SO2}=Sulfur dioxide removed, lb/day, as calculated below using Eq. G–7.

F_u=1.0, the calcium to sulfur stoichiometric ratio.

and

$$W_{SO_2} = SO_{2o} \frac{\%R}{(100-\%R)} \qquad (Eq.\ G\text{-}7)$$

(Eq. G–7)

where:

WSO_2= Weight of sulfur dioxide removed, lb/day.

SO_{2O}= SO_2 mass emissions monitored at the outlet, lb/day, as calculated using the equations and procedures in section 2 of appendix F of this attachment.

%R = Overall percentage SO_2 emissions removal efficiency, calculated using equations such as those in EPA Method 19 in appendix A to 40 CFR part 60, and using daily instead of annual average emission rates.

3.2 When a sorbent material other than limestone is used, modify the equations, methods, and procedures in section 3.1 of this appendix as follows to estimate daily CO_2mass emissions from sorbent (in tons).

3.2.1 Determine a site-specific value for F_u, defined as the ratio of the number of moles of CO_2 released upon capture of one mole of SO_2, using methods and procedures satisfactory to the DEQ. Use this value of F_u (instead of 1.0) in either equation G–5 or equation G–6.

3.2.2 When using equation G–5, replace MW_{CaCO3}, the molecular weight of calcium carbonate, with the molecular weight of the sorbent material that participates in the reaction to capture SO_2 and that releases CO_2, and replace W_{CaCO3}, the amount of calcium carbonate used (in tons/day), with the amount of sorbent material used (in tons/day).

4. Procedures for Estimating Total CO_2 Emissions

The permittee shall use the following equation to obtain total daily CO_2 mass emissions (in tons) as the sum of combustion-related emissions and sorbent-related emissions.

$$W_t = W_{CO2} + SE_{CO2}$$

(Eq. G–8)

where,

W_t= Estimated total CO_2 mass emissions, tons/day.

W_{CO2}= CO_2 emitted from fuel combustion, tons/day.

SE_{CO2}= CO_2 emitted from sorbent, tons/day.

5. Missing Data Substitution Procedures for Fuel Analytical Data

Use the following procedures to substitute for missing fuel analytical data used to calculate CO_2 mass emissions under this appendix.

5.1–5.1.2[Reserved]

5.2 Missing Carbon Content Data

Use the following procedures to substitute for missing carbon content data.

5.2.1 In all cases (i.e., for weekly coal samples) when carbon content data is missing, report the appropriate default value from Table G–1.

5.2.2 The missing data values in Table G–1 shall be reported whenever the results of a required sample of fuel carbon content are either missing or invalid. The substitute data value shall be used until the next valid carbon content sample is obtained.

TABLE G-1. -- MISSING DATA SUBSTITUTION PROCEDURES FOR MISSING CARBON CONTENT DATA

Parameter	Missing data value
Oil and coal carbon content	Most recent, previous carbon content value available for that type of coal, grade of oil, or default value, in this table
Gas carbon content	Most recent, previous carbon content value available for that type of gaseous fuel, or default value, in this table
Default coal carbon content	Anthracite: 90.0 percent
	Bituminous: 85.0 percent
	Subbituminous/Lignite: 75.0 percent
Default oil carbon content	90.0 percent
Default gas carbon content	Natural gas: 75.0 percent
	Other gaseous fuels: 90.0 percent

Appendix H to Attachment—Revised Traceability Protocol No. 1 [Reserved]

Appendix I to Attachment—Optional F—Factor/Fuel Flow Method [Reserved]

Appendix J to Attachment—Compliance Dates for Revised Recordkeeping Requirements and Missing Data Procedures [Reserved]

Appendix K to Attachment—Quality Assurance and Operating Procedures for Sorbent Trap Monitoring Systems

1.0 Scope and Application

This appendix specifies sampling, and analytical, and quality-assurance criteria and procedures for the performance-based monitoring of vapor-phase mercury (Hg) emissions in combustion flue gas streams, using a sorbent trap monitoring system (as defined in 40 CFR 72.2). The principle employed is continuous sampling using in-stack sorbent media coupled with analysis of the integrated samples. The performance-based approach of this appendix allows for use of various suitable sampling and analytical technologies while maintaining a specified and documented level of data quality through performance criteria. Persons using this appendix should have a thorough working knowledge of EPA Methods 1, 2, 3, 4 and 5 in appendices A–1 through A–3 to 40 CFR part 60, as well as the determinative technique selected for analysis.

1.1 Analytes.

The analyte measured by these procedures and specifications is total vapor-phase Hg in the flue gas, which represents the sum of elemental Hg (Hg^0, CAS Number 7439–97–6) and oxidized forms of Hg, in mass concentration units of micrograms per dry standard cubic meter (μgm/dscm).

1.2 Applicability.

These performance criteria and procedures are applicable to monitoring of vapor-phase Hg emissions under relatively low-dust conditions (*i.e.* , sampling in the stack after all pollution control devices), from the CFB boilers. Individual sample collection times can range from 30 minutes to several days in duration, depending on the Hg concentration in the stack. The monitoring system must achieve the performance criteria specified in Section 8 of this appendix and the sorbent media capture ability must not be exceeded. The sampling rate must be maintained at a constant proportion to the total stack flowrate to ensure representativeness of the sample collected. Failure to achieve certain performance criteria will result in invalid Hg emissions monitoring data.

2.0 Principle.

Known volumes of flue gas are extracted from a stack or duct through paired, in-stack, pre-spiked sorbent media traps at an appropriate nominal flow rate. Collection of Hg on the sorbent media in the stack mitigates potential loss of Hg during transport through a probe/sample line. Paired train sampling is required to determine measurement precision and verify acceptability of the measured emissions data.

The sorbent traps are recovered from the sampling system, prepared for analysis, as needed, and analyzed by any suitable determinative technique that can meet the performance criteria. A section of each sorbent trap is spiked with Hg^0 prior to sampling. This section is analyzed separately and the recovery value is used to correct the individual Hg sample for measurement bias.

3.0 Clean Handling and Contamination.

To avoid Hg contamination of the samples, special attention should be paid to cleanliness during transport, field handling, sampling, recovery, and laboratory analysis, as well as during preparation of the sorbent cartridges. Collection and analysis of blank samples (field, trip, lab) is useful in verifying the absence of contaminant Hg.

4.0 Safety.

4.1 Site hazards.

Site hazards must be thoroughly considered in advance of applying these procedures/specifications in the field; advance coordination with the site is critical to understand the conditions and applicable safety policies. At a minimum, portions of the sampling system will be hot, requiring appropriate gloves, long sleeves, and caution in handling this equipment.

4.2 Laboratory safety policies.

Laboratory safety policies should be in place to minimize risk of chemical exposure and to properly handle waste disposal. Personnel shall wear appropriate laboratory attire according to a Chemical Hygiene Plan established by the laboratory.

4.3 Toxicity or carcinogenicity.

The toxicity or carcinogenicity of any reagents used must be considered. Depending upon the sampling and analytical technologies selected, this measurement may involve hazardous materials, operations, and equipment and this appendix does not address all of the safety problems associated with implementing this approach. It is the responsibility of the user to establish appropriate safety and health practices and determine the applicable regulatory limitations prior to performance. Any chemical should be regarded as a potential health hazard and exposure to these compounds should be minimized. Chemists should refer to the Material Safety Data Sheet (MSDS) for each chemical used.

4.4 Wastes.

Any wastes generated by this procedure must be disposed of according to a hazardous materials management plan that details and tracks various waste streams and disposal procedures.

5.0 Equipment and Supplies.

The following list is presented as an example of key equipment and supplies likely required to perform vapor-phase Hg monitoring using a sorbent trap monitoring system. It is recognized that additional equipment and supplies may be needed. Collection of paired samples is required. Also required are a certified stack gas volumetric flow monitor that meets the requirements of 40 CFR 75.10 and an acceptable means of correcting for the stack gas moisture content, *i.e.* , either by using data from a certified continuous moisture monitoring system or by using an approved default moisture value (see 40 CFR 75.11(b)).

5.1 Sorbent Trap Monitoring System.

A typical sorbent trap monitoring system is shown in Figure K–1. The monitoring system shall include the following components:

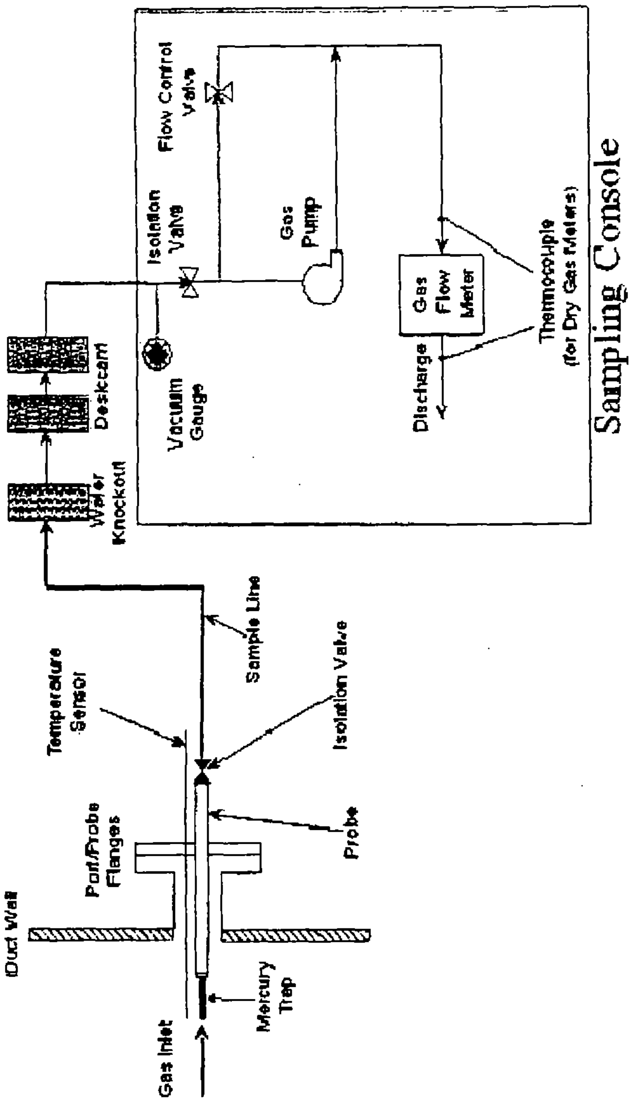
Flow Control Valve
Isolation Valve
Gas Pump
Gas Flow Meter
Thermocouple (for Dry Gas Meters)
Sampling Console
Discharge
Vacuum Gauge
Desiccant
Water Knockout
Sample Line
Isolation Valve
Temperature Sensor
Port/Probe Flanges
Probe
Duct Wall
Gas Inlet
Mercury Trap

Figure K-1. Typical Sorbent Trap Monitoring System

5.1.1 Sorbent Traps.

The sorbent media used to collect Hg must be configured in a trap with three distinct and identical segments or sections, connected in series, that are amenable to separate analyses. Section 1 is designated for primary capture of gaseous Hg. Section 2 is designated as a backup section for determination of vapor-phase Hg breakthrough. Section 3 is designated for QA/QC purposes where this section shall be spiked with a known amount of gaseous Hg^0 prior to sampling and later analyzed to determine recovery efficiency. The sorbent media may be any collection material (*e.g.* , carbon, chemically-treated filter, etc.) capable of quantitatively capturing and recovering for subsequent analysis, all gaseous forms of Hg for the intended application. Selection of the sorbent media shall be based on the material's ability to achieve the performance criteria contained in Section 8 of this appendix as well as the sorbent's vapor-phase Hg capture efficiency for the emissions matrix and the expected sampling duration at the test site. The sorbent media must be obtained from a source that can demonstrate the quality assurance and control necessary to ensure consistent reliability. The paired sorbent traps are supported on a probe (or probes) and inserted directly into the flue gas stream.

5.1.2 Sampling Probe Assembly.

Each probe assembly shall have a leak-free attachment to the sorbent trap(s). Each sorbent trap must be mounted at the entrance of or within the probe such that the gas sampled enters the trap directly. Each probe/sorbent trap assembly must be heated to a temperature sufficient to prevent liquid condensation in the sorbent trap(s). Auxiliary heating is required only where the stack temperature is too low to prevent condensation. Use a calibrated thermocouple to monitor the stack temperature. A single probe capable of operating the paired sorbent traps may be used. Alternatively, individual probe/sorbent trap assemblies may be used, provided that the individual sorbent traps are co-located to ensure representative Hg monitoring and are sufficiently separated to prevent aerodynamic interference.

5.1.3 Moisture Removal Device

A robust moisture removal device or system, suitable for continuous duty (such as a Peltier cooler), shall be used to remove water vapor from the gas stream prior to entering the gas flow meter.

5.1.4 Vacuum Pump.

Use a leak-tight, vacuum pump capable of operating within the candidate system's flow range.

5.1.5 Gas Flow Meter

A gas flow meter (such as a dry gas meter, thermal mass flow meter, or other suitable measurement device) shall be used to determine the total sample volume on a dry basis, in units of standard cubic meters. The meter must be sufficiently accurate to measure the total sample volume to within 2 percent and must be calibrated at selected flow rates across the range of sample flow rates at which the sorbent trap monitoring system typically operates. The gas flow meter shall be equipped with any necessary auxiliary measurement devices (e.g., temperature sensors, pressure measurement devices) needed to correct the sample volume to standard conditions.

5.1.6 Sample Flow Rate Meter and Controller.

Use a flow rate indicator and controller for maintaining necessary sampling flow rates.

5.1.7 Temperature Sensor.

Same as Section 6.1.1.7 of EPA Method 5 in appendix A–3 to 40 CFR part 60.

5.1.8 Barometer.

Same as Section 6.1.2 of EPA Method 5 in appendix A–3 to 40 CFR part 60.

5.1.9 Data Logger (Optional).

Device for recording associated and necessary ancillary information (*e.g.* , temperatures, pressures, flow, time, etc.).

5.2 Gaseous Hg^0 Sorbent Trap Spiking System.

A known mass of gaseous Hg^0 must be spiked onto section 3 of each sorbent trap prior to sampling. Any approach capable of quantitatively delivering known masses of Hg^0 onto sorbent traps is acceptable. Several technologies or devices are available to meet this objective. Their practicality is a function of Hg mass spike levels. For low levels, NIST-certified or NIST-traceable gas generators or tanks may be suitable, but will likely require long preparation times. A more practical, alternative system, capable of delivering almost any mass required, makes use of NIST-certified or NIST-traceable Hg salt solutions (*e.g.* , $Hg(NO_3)_2$). With this system, an aliquot of known volume and concentration is added to a reaction vessel containing a reducing agent (*e.g.* , stannous chloride); the Hg salt solution is reduced to Hg^0 and purged onto section 3 of the sorbent trap using an impinger sparging system.

5.3 Sample Analysis Equipment.

Any analytical system capable of quantitatively recovering and quantifying total gaseous Hg from sorbent media is acceptable provided that the analysis can meet the performance criteria in Section 8 of this procedure. Candidate recovery techniques include leaching, digestion, and thermal desorption. Candidate analytical techniques include ultraviolet atomic fluorescence (UV AF); ultraviolet atomic absorption (UV AA), with and without gold trapping; and in situ X-ray fluorescence (XRF) analysis.

6.0 Reagents and Standards.

Only NIST-certified or NIST-traceable calibration gas standards and reagents shall be used for the tests and procedures required under this appendix.

7.0 Sample Collection and Transport.

7.1 Pre-Test Procedures.

7.1.1 Selection of Sampling Site.

Sampling site information should be obtained in accordance with EPA Method 1 in appendix A–1 to 40 CFR part 60. Identify a monitoring location representative of source Hg emissions. Locations shown to be free of stratification through measurement traverses for gases such as SO_2 and NO_X may be one such approach. An estimation of the expected stack Hg concentration is required to establish a target sample flow rate, total gas sample volume, and the mass of Hg^0 to be spiked onto section 3 of each sorbent trap.

7.1.2 Pre-sampling Spiking of Sorbent Traps.

Based on the estimated Hg concentration in the stack, the target sample rate and the target sampling duration, calculate the expected mass loading for section 1 of each sorbent trap (for an example calculation, see section 11.1 of this appendix). The pre-sampling spike to be added to section 3 of each sorbent trap shall be within ±50 percent of the expected section 1 mass loading. Spike section 3 of each sorbent trap at this level, as described in section 5.2 of this appendix. For each sorbent trap, keep an official record of the mass of Hg^0 added to section 3. This record shall include, at a minimum, the ID number of the trap, the date and time of the spike, the name of the analyst performing the procedure, the mass of Hg^0 added to section 3 of the trap (μgm), and the supporting calculations. This record shall be maintained in a format suitable for inspection and audit and shall be made available to the regulatory agencies upon request.

7.1.3 Pre-test Leak Check

Perform a leak check with the sorbent traps in place. Draw a vacuum in each sample train. Adjust the vacuum in the sample train to □15" Hg. Using the gas flow meter, determine leak rate. The leakage rate must not exceed 4 percent of the target sampling rate. Once the leak check passes this criterion, carefully release the vacuum in the sample train then seal the sorbent trap inlet until the probe is ready for insertion into the stack or duct.

7.1.4 Determination of Flue Gas Characteristics.

Determine or measure the flue gas measurement environment characteristics (gas temperature, static pressure, gas velocity, stack moisture, etc.) in order to determine ancillary requirements such as probe heating requirements (if any), initial sample rate, proportional sampling conditions, moisture management, etc.

7.2 Sample Collection.

7.2.1 Remove the plug from the end of each sorbent trap and store each plug in a clean sorbent trap storage container. Remove the stack or duct port cap and insert the probe(s). Secure the probe(s) and ensure that no leakage occurs between the duct and environment.

7.2.2 Record initial data including the sorbent trap ID, start time, starting dry gas meter readings, initial temperatures, set-points, and any other appropriate information.

7.2.3 Flow Rate Control

Set the initial sample flow rate at the target value from section 7.1.1 of this appendix. Record the initial gas flow meter reading, stack temperature (if needed to convert to standard conditions), meter temperatures (if needed), etc. Then, for every operating hour during the sampling period, record the date and time, the sample flow rate, the gas flow meter reading, the stack temperature (if needed), the flow meter temperatures (if needed), temperatures of heated equipment such as the vacuum lines and the probes (if heated), and the sampling system vacuum readings. Also, record the stack gas flow rate, as measured by the certified flow monitor, and the ratio of the stack gas flow rate to the sample flow rate. Adjust the sampling flow rate to maintain proportional sampling, i.e., keep the ratio of the stack gas flow rate to sample flow rate constant, to within ±25 percent of the reference ratio from the first hour of the data collection period (see section 11 of this appendix). The sample flow rate through a sorbent trap monitoring system during any hour (or portion of an hour) in which the unit is not operating shall be zero.

7.2.4 Stack Gas Moisture Determination.

Determine stack gas moisture using a continuous moisture monitoring system, as described in 40 CFR 75.11(b). Alternatively, the permittee may use the appropriate fuel-specific moisture default value provided in 40 CFR 75.11, or a site-specific moisture default value approved by petition under 40 CFR 75.66.

7.2.5 Essential Operating Data

Obtain and record any essential operating data for the facility during the test period, e.g., the barometric pressure for correcting the sample volume measured by a dry gas meter to standard conditions. At the end of the data collection period, record the final gas flow meter reading and the final values of all other essential parameters.

7.2.6 Post Test Leak Check.

When sampling is completed, turn off the sample pump, remove the probe/sorbent trap from the port and carefully re-plug the end of each sorbent trap. Perform a leak check with the sorbent traps in place, at the maximum vacuum reached during the sampling period. Use the same general approach described in section 7.1.3 of this appendix. Record the leakage rate and vacuum. The leakage rate must not exceed 4 percent of the average sampling rate for the data collection period. Following the leak check, carefully release the vacuum in the sample train.

7.2.7 Sample Recovery.

Recover each sampled sorbent trap by removing it from the probe, sealing both ends. Wipe any deposited material from the outside of the sorbent trap. Place the sorbent trap into an appropriate sample storage container and store/preserve in appropriate manner.

7.2.8 Sample Preservation, Storage, and Transport.

While the performance criteria of this approach provide for verification of appropriate sample handling, it is still important that the user consider, determine, and plan for suitable sample preservation, storage, transport, and holding times for these measurements. Therefore, procedures in ASTM D6911–03 "Standard Guide for Packaging and Shipping Environmental Samples for Laboratory Analysis" (incorporated by reference, see 40 CFR 75.6) shall be followed for all samples.

7.2.9 Sample Custody.

Proper procedures and documentation for sample chain of custody are critical to ensuring data integrity. The chain of custody procedures in ASTM D4840–99 (reapproved 2004) "Standard Guide for Sample Chain-of-Custody Procedures" (incorporated by reference, see 40 CFR 75.6) shall be followed for all samples (including field samples and blanks).

8.0 Quality Assurance and Quality Control.

Table K–1 summarizes the QA/QC performance criteria that are used to validate the Hg emissions data from sorbent trap monitoring systems, including the relative accuracy test audit (RATA) requirement (see 40 CFR 75.20(c)(9), section 6.5.7 of appendix A to this attachment, and section 2.3 of appendix B to this attachment). Except as provided in 40 CFR 75.15(h) and as otherwise indicated in Table K–1, failure to achieve these performance criteria will result in invalidation of Hg emissions data.

Table K–1.—Quality Assurance/Quality Control Criteria for Sorbent Trap Monitoring Systems

QA/QC test or specification	Acceptance criteria	Frequency	Consequences if not met
Pre-test leak check	≤4% of target sampling rate	Prior to sampling	Sampling shall not commence until the leak check is passed.
Post-test leak check	≤4% of average sampling rate	After sampling	** See *Note* , below.
Ratio of stack gas flow rate to sample flow rate	No more than 5% of the hourly ratios or 5 hourly ratios (whichever is less restrictive) may deviate from the reference ratio by more than ± 25%	Every hour throughout data collection period	** See *Note* , below.

QA/QC test or specification	Acceptance criteria	Frequency	Consequences if not met
Sorbent trap section 2 break-through	≤5% of Section 1 Hg mass	Every sample	** See *Note* , below.
Paired sorbent trap agreement	≤10% Relative Deviation (RD) if the average concentration is > 1.0 µg/m^3 ≤ 20% RD if the average concentration is ≤ 1.0 µg/m^3 Results are also acceptable if absolute difference between concentrations from paired traps is ≤ 0.03 µg/m^3	Every sample	Either invalidate the data from the paired traps or report the results from the trap with the higher Hg concentration.
Spike Recovery Study	Average recovery between 85% and 115% for each of the 3 spike concentration levels	Prior to analyzing field samples and prior to use of new sorbent media	Field samples shall not be analyzed until the percent recovery criteria has been met
Multipoint analyzer calibration	Each analyzer reading within ± 10% of true value and $r^2 \geq 0.99$	On the day of analysis, before analyzing any field samples	Recalibrate until successful.
Analysis of independent calibration standard	Within ± 10% of true value	Following daily calibration, prior to analyzing field samples	Recalibrate and repeat independent standard analysis until successful.
Spike recovery from section 3 of sorbent trap	75–125% of spike amount	Every sample	** See *Note* , below.
RATA	RA ≤ 20.0% *or* Mean difference ≤ 1.0 µg/dscm for low emitters	For initial certification and annually thereafter	Data from the system are invalidated until a RATA is passed.

QA/QC test or specification	Acceptance criteria	Frequency	Consequences if not met
Gas flow meter calibration	Calibration factor (Y) within ± 5% of average value from the most recent 3-point calibration	At three settings prior to initial use and at least quarterly at one setting thereafter. For mass flow meters, initial calibration with stack gas is required	Recalibrate the meter at three orifice settings to determine a new value of Y.
Temperature sensor calibration	Absolute temperature measured by sensor within ± 1.5% of a reference sensor	Prior to initial use and at least quarterly thereafter	Recalibrate. Sensor may not be used until specification is met.
Barometer calibration	Absolute pressure measured by instrument within ± 10 mm Hg of reading with a mercury barometer	Prior to initial use and at least quarterly thereafter	Recalibrate. Instrument may not be used until specification is met.

**Note: If both traps fail to meet the acceptance criteria, the data from the pair of traps are invalidated. However, if only one of the paired traps fails to meet this particular acceptance criterion and the other sample meets all of the applicable QA criteria, the results of the valid trap may be used for reporting under this attachment, provided that the measured Hg concentration is multiplied by a factor of 1.111. When the data from both traps are invalidated and quality-assured data from a certified backup monitoring system, reference method, or approved alternative monitoring system are unavailable, missing data substitution must be used.

9.0 Calibration and Standardization.

9.1 Only NIST-certified and NIST-traceable calibration standards (i.e., calibration gases, solutions, etc.) shall be used for the spiking and analytical procedures in this appendix.

9.2 Gas Flow Meter Calibration

9.2.1 Preliminaries. The manufacturer or supplier of the gas flow meter should perform all necessary set-up, testing, programming, etc., and should provide the end user with any necessary instructions, to ensure that the meter will give an accurate readout of dry gas volume in standard cubic meters for the particular field application.

9.2.2 Initial Calibration. Prior to its initial use, a calibration of the flow meter shall be performed. The initial calibration may be done by the manufacturer, by the equipment supplier, or by the end user. If the flow meter is volumetric in nature (e.g., a dry gas meter), the manufacturer, equipment supplier, or end user may perform a direct volumetric calibration using any gas. For a mass flow meter, the manufacturer, equipment supplier, or end user may calibrate the meter using a bottled gas mixture containing 12 ± 0.5% CO_2, 7 ± 0.5% O_2, and balance N_2, or these same gases in proportions more representative of the expected stack gas composition. Mass flow meters may also be initially calibrated on-site, using actual stack gas.

9.2.2.1 Initial Calibration Procedures. Determine an average calibration factor (Y) for the gas flow meter, by calibrating it at three sample flow rate settings covering the range of sample flow rates at which the sorbent trap monitoring system typically operates. You may either follow the procedures in section 10.3.1 of EPA Method 5 in appendix A–3 to 40 CFR part 60 or the procedures in section 16 of EPA Method 5 in appendix A–3 to 40 CFR part 60. If a dry gas meter is being calibrated, use at least five revolutions of the meter at each flow rate.

9.2.2.2 Alternative Initial Calibration Procedures. Alternatively, you may perform the initial calibration of the gas flow meter using a reference gas flow meter (RGFM). The RGFM may either be: (1) A wet test meter calibrated according to section 10.3.1 of EPA Method 5 in appendix A–3 to 40 CFR part 60; (2) a gas flow metering device calibrated at multiple flow rates using the procedures in section 16 of EPA Method 5 in appendix A–3 to 40 CFR part 60; or (3) a NIST–traceable calibration device capable of measuring volumetric flow to an accuracy of 1 percent. To calibrate the gas flow meter using the RGFM, proceed as follows: While the sorbent trap monitoring system is sampling the actual stack gas or a compressed gas mixture that simulates the stack gas composition (as applicable), connect the RGFM to the discharge of the system. Care should be taken to minimize the dead volume between the sample flow meter being tested and the RGFM. Concurrently measure dry gas volume with the RGFM and the flow meter being calibrated the for a minimum of 10 minutes at each of three flow rates covering the typical range of operation of the sorbent trap monitoring system. For each 10-minute (or longer) data collection period, record the total sample volume, in units of dry standard cubic meters (dscm), measured by the RGFM and the gas flow meter being tested.

9.2.2.3 Initial Calibration Factor. Calculate an individual calibration factor Yi at each tested flow rate from section 9.2.2.1 or 9.2.2.2 of this appendix (as applicable), by taking the ratio of the reference sample volume to the sample volume recorded by the gas flow meter. Average the three Yi values, to determine Y, the calibration factor for the flow meter. Each of the three individual values of Yi must be within ±0.02 of Y. Except as otherwise provided in sections 9.2.2.4 and 9.2.2.5 of this appendix, use the average Y value from the three level calibration to adjust all subsequent gas volume measurements made with the gas flow meter.

9.2.2.4 Initial On-Site Calibration Check. For a mass flow meter that was initially calibrated using a compressed gas mixture, an on-site calibration check shall be performed before using the flow meter to provide data for this attachment. While sampling stack gas, check the calibration of the flow meter at one intermediate flow rate typical of normal operation of the monitoring system. Follow the basic procedures in section 9.2.2.1 or 9.2.2.2 of this appendix. If the on-site calibration check shows that the value of Yi, the calibration factor at the tested flow rate, differs by more than 5 percent from the value of Y obtained in the initial calibration of the meter, repeat the full 3-level calibration of the meter using stack gas to determine a new value of Y, and apply the new Y value to all subsequent gas volume measurements made with the gas flow meter.

9.2.2.5 Ongoing Quality Assurance. Recalibrate the gas flow meter quarterly at one intermediate flow rate setting representative of normal operation of the monitoring system. Follow the basic procedures in section 9.2.2.1 or 9.2.2.2 of this appendix. If a quarterly recalibration shows that the value of Yi, the calibration factor at the tested flow rate, differs from the current value of Y by more than 5 percent, repeat the full 3-level calibration of the meter to determine a new value of Y, and apply the new Y value to all subsequent gas volume measurements made with the gas flow meter.

9.3 Thermocouples and Other Temperature Sensors.

Use the procedures and criteria in Section 10.3 of EPA Method 2 in appendix A–1 to 40 CFR part 60 to calibrate in-stack temperature sensors and thermocouples. Dial thermometers shall be calibrated against mercury-in-glass thermometers. Calibrations must be performed prior to initial use and at least quarterly thereafter. At each calibration point, the absolute temperature measured by the temperature sensor must agree to within ±1.5 percent of the temperature measured with the reference sensor, otherwise the sensor may not continue to be used.

9.4 Barometer.

Calibrate against a mercury barometer. Calibration must be performed prior to initial use and at least quarterly thereafter. At each calibration point, the absolute pressure measured by the barometer must agree to within ±10 mm Hg of the pressure measured by the mercury barometer, otherwise the barometer may not continue to be used.

9.5 Other Sensors and Gauges.

Calibrate all other sensors and gauges according to the procedures specified by the instrument manufacturer(s).

9.6 Analytical System Calibration.

See section 10.1 of this appendix.

10.0 Analytical Procedures.

The analysis of the Hg samples may be conducted using any instrument or technology capable of quantifying total Hg from the sorbent media and meeting the performance criteria in section 8 of this appendix.

10.1 Analyzer System Calibration.

Perform a multipoint calibration of the analyzer at three or more upscale points over the desired quantitative range (multiple calibration ranges shall be calibrated, if necessary). The field samples analyzed must fall within a calibrated, quantitative range and meet the necessary performance criteria. For samples that are suitable for aliquotting, a series of dilutions may be needed to ensure that the samples fall within a calibrated range. However, for sorbent media samples that are consumed during analysis (*e.g.*, thermal desorption techniques), extra care must be taken to ensure that the analytical system is appropriately calibrated prior to sample analysis. The calibration curve range(s) should be determined based on the anticipated level of Hg mass on the sorbent media. Knowledge of estimated stack Hg concentrations and total sample volume may be required prior to analysis. The calibration curve for use with the various analytical techniques (*e.g.*, UV AA, UV AF, and XRF) can be generated by directly introducing standard solutions into the analyzer or by spiking the standards onto the sorbent media and then introducing into the analyzer after preparing the sorbent/standard according to the particular analytical technique. For each calibration curve, the value of the square of the linear correlation coefficient, *i.e.*, r^2, must be ≥ 0.99, and the analyzer response must be within ±10 percent of reference value at each upscale calibration point. Calibrations must be performed on the day of the analysis, before analyzing any of the samples. Following calibration, an independently prepared standard (not from same calibration stock solution) shall be analyzed. The measured value of the independently prepared standard must be within ±10 percent of the expected value.

10.2 Sample Preparation.

Carefully separate the three sections of each sorbent trap. Combine for analysis all materials associated with each section, *i.e.*, any supporting substrate that the sample gas passes through prior to entering a media section (*e.g.*, glass wool, polyurethane foam, etc.) must be analyzed with that segment.

10.3 Spike Recovery Study.

Before analyzing any field samples, the laboratory must demonstrate the ability to recover and quantify Hg from the sorbent media by performing the following spike recovery study for sorbent media traps spiked with elemental mercury.

Using the procedures described in sections 5.2 and 11.1 of this appendix, spike the third section of nine sorbent traps with gaseous Hg^0, *i.e.*, three traps at each of three different mass loadings, representing the range of masses anticipated in the field samples. This will yield a 3 × 3 sample matrix. Prepare and analyze the third section of each spiked trap, using the techniques that will be used to prepare and analyze the field samples. The average recovery for each spike concentration must be between 85 and 115 percent. If multiple types of sorbent media are to be analyzed, a separate spike recovery study is required for each sorbent material. If multiple ranges are calibrated, a separate spike recovery study is required for each range.

10.4 Field Sample Analysis

Analyze the sorbent trap samples following the same procedures that were used for conducting the spike recovery study. The three sections of each sorbent trap must be analyzed separately (i.e., section 1, then section 2, then section 3). Quantify the total mass of Hg for each section based on analytical system response and the calibration curve from section 10.1 of this appendix. Determine the spike recovery from sorbent trap section 3. The spike recovery must be no less than 75 percent and no greater than 125 percent. To report the final Hg mass for each trap, add together the Hg masses collected in trap sections 1 and 2.

11.0 Calculations and Data Analysis.

11.1 Calculation of Pre-Sampling Spiking Level.

Determine sorbent trap section 3 spiking level using estimates of the stack Hg concentration, the target sample flow rate, and the expected sample duration. First, calculate the expected Hg mass that will be collected in section 1 of the trap. The pre-sampling spike must be within ±50 percent of this mass. Example calculation: For an estimated stack Hg concentration of 5 $\mu gm/m^3$, a target sample rate of 0.30 L/min, and a sample duration of 5 days:

$$(0.30\ L/min)\ (1440\ min/day)\ (5\ days)\ (10^{-3} m^3/liter)\ (5 \mu gm/m^3) = 10.8\ \mu gm$$

A pre-sampling spike of 10.8 μgm ±50 percent is, therefore, appropriate.

11.2 Calculations for Flow-Proportional Sampling.

For the first hour of the data collection period, determine the reference ratio of the stack gas volumetric flow rate to the sample flow rate, as follows:

$$R_{ref} = \frac{KQ_{ref}}{F_{ref}} \qquad (Eq.\ K\text{-}1)$$

Where:

R_{ref}= Reference ratio of hourly stack gas flow rate to hourly sample flow rate

Q_{ref}= Average stack gas volumetric flow rate for first hour of collection period, adjusted for bias, if necessary, according to section 7.6.5 of appendix A to this attachment, (scfh)

F_{ref}= Average sample flow rate for first hour of the collection period, in appropriate units (*e.g.,* liters/min, cc/min, dscm/min)

K = Power of ten multiplier, to keep the value of R_{ref} between 1 and 100. The appropriate K value will depend on the selected units of measure for the sample flow rate.

Then, for each subsequent hour of the data collection period, calculate ratio of the stack gas flow rate to the sample flow rate using the equation K–2:

$$R_h = \frac{KQ_h}{F_h} \qquad \text{(Eq. K-2)}$$

Where:

R_h= Ratio of hourly stack gas flow rate to hourly sample flow rate

Q_h= Average stack gas volumetric flow rate for the hour, adjusted for bias, if necessary, according to section 7.6.5 of appendix A to this attachment, (scfh)

F_h= Average sample flow rate for the hour, in appropriate units (*e.g.*, liters/min, cc/min, dscm/min)

K = Power of ten multiplier, to keep the value of R_h between 1 and 100. The appropriate K value will depend on the selected units of measure for the sample flow rate and the range of expected stack gas flow rates.

Maintain the value of R_h within ±25 percent of R_{ref} throughout the data collection period.

11.3 Calculation of Spike Recovery.

Calculate the percent recovery of each section 3 spike, as follows:

$$\%R = \frac{M_3}{M_s} \times 100 \qquad \text{(Eq. K-3)}$$

Where:

%R = Percentage recovery of the pre-sampling spike

M_3= Mass of Hg recovered from section 3 of the sorbent trap, (μgm)

M_s= Calculated Hg mass of the pre-sampling spike, from section 7.1.2 of this appendix, (μgm)

11.4 Calculation of Breakthrough.

Calculate the percent breakthrough to the second section of the sorbent trap, as follows:

$$\%B = \frac{M_2}{M_1} \times 100 \qquad \text{(Eq. K-4)}$$

Where:

%B = Percent breakthrough

M_2= Mass of Hg recovered from section 2 of the sorbent trap, (μgm)

M_1= Mass of Hg recovered from section 1 of the sorbent trap, (μgm)

11.5 [Reserved]

11.6 Calculation of Hg Concentration

Calculate the Hg concentration for each sorbent trap, using the following equation:

$$C = \frac{M^*}{V_t} \qquad \text{(Eq. K-5)}$$

Where:

C = Concentration of Hg for the collection period, (μgm/dscm)

M^* = Total mass of Hg recovered from sections 1 and 2 of the sorbent trap, (μg)

Vt= Total volume of dry gas metered during the collection period, (dscm). For the purposes of this appendix, standard temperature and pressure are defined as 20 °C and 760 mm Hg, respectively.

11.7 Calculation of Paired Trap Agreeement

Calculate the relative deviation (RD) between the Hg concentrations measured with the paired sorbent traps:

$$RD = \frac{|C_a - C_b|}{C_a + C_b} \times 100 \qquad \text{(Eq. K-6)}$$

Where:

RD = Relative deviation between the Hg concentrations from traps "a" and "b" (percent)

Ca= Concentration of Hg for the collection period, for sorbent trap "a" (μgm/dscm)

Cb= Concentration of Hg for the collection period, for sorbent trap "b" (μgm/dscm)

11.8 Calculation of Hg Mass Emissions.

To calculate Hg mass emissions, follow the procedures in section 9.1.2 of appendix F to this attachment. Use the average of the two Hg concentrations from the paired traps in the calculations, except as provided in 40 CFR 75.15(h) or in Table K–1.

12.0 Method Performance.

These monitoring criteria and procedures have been applied to coal-fired utility boilers (including units with post-combustion emission controls), having vapor-phase Hg concentrations ranging from 0.03 μgm/dscm to 100 μgm/dscm.

Title 40: Protection of Environment

PART 63—NATIONAL EMISSION STANDARDS FOR HAZARDOUS AIR POLLUTANTS FOR SOURCE CATEGORIES

Subpart A—General Provisions

Source: 59 FR 12430, Mar. 16, 1994, unless otherwise noted.

§ 63.1 Applicability.

(a) *General.* (1) Terms used throughout this part are defined in §63.2 or in the Clean Air Act (Act) as amended in 1990, except that individual subparts of this part may include specific definitions in addition to or that supersede definitions in §63.2.

(2) This part contains national emission standards for hazardous air pollutants (NESHAP) established pursuant to section 112 of the Act as amended November 15, 1990. These standards regulate specific categories of stationary sources that emit (or have the potential to emit) one or more hazardous air pollutants listed in this part pursuant to section 112(b) of the Act. This section explains the applicability of such standards to sources affected by them. The standards in this part are independent of NESHAP contained in 40 CFR part 61. The NESHAP in part 61 promulgated by signature of the Administrator before November 15, 1990 (i.e., the date of enactment of the Clean Air Act Amendments of 1990) remain in effect until they are amended, if appropriate, and added to this part.

(3) No emission standard or other requirement established under this part shall be interpreted, construed, or applied to diminish or replace the requirements of a more stringent emission limitation or other applicable requirement established by the Administrator pursuant to other authority of the Act (section 111, part C or D or any other authority of this Act), or a standard issued under State authority. The Administrator may specify in a specific standard under this part that facilities subject to other provisions under the Act need only comply with the provisions of that standard.

(4)(i) Each relevant standard in this part 63 must identify explicitly whether each provision in this subpart A is or is not included in such relevant standard.

(ii) If a relevant part 63 standard incorporates the requirements of 40 CFR part 60, part 61 or other part 63 standards, the relevant part 63 standard must identify explicitly the applicability of each corresponding part 60, part 61, or other part 63 subpart A (General) provision.

(iii) The General Provisions in this subpart A do not apply to regulations developed pursuant to section 112(r) of the amended Act, unless otherwise specified in those regulations.

(5) [Reserved]

(6) To obtain the most current list of categories of sources to be regulated under section 112 of the Act, or to obtain the most recent regulation promulgation schedule established pursuant to section 112(e) of the Act, contact the Office of the Director, Emission Standards Division, Office of Air Quality Planning and Standards, U.S. EPA (MD–13), Research Triangle Park, North Carolina 27711.

(7)–(9) [Reserved]

(10) For the purposes of this part, time periods specified in days shall be measured in calendar days, even if the word "calendar" is absent, unless otherwise specified in an applicable requirement.

(11) For the purposes of this part, if an explicit postmark deadline is not specified in an applicable requirement for the submittal of a notification, application, test plan, report, or other written communication to the Administrator, the owner or operator shall postmark the submittal on or before the number of days specified in the applicable requirement. For example, if a notification must be submitted 15 days before a particular event is scheduled to take place, the notification shall be postmarked on or before 15 days

preceding the event; likewise, if a notification must be submitted 15 days after a particular event takes place, the notification shall be postmarked on or before 15 days following the end of the event. The use of reliable non-Government mail carriers that provide indications of verifiable delivery of information required to be submitted to the Administrator, similar to the postmark provided by the U.S. Postal Service, or alternative means of delivery agreed to by the permitting authority, is acceptable.

(12) Notwithstanding time periods or postmark deadlines specified in this part for the submittal of information to the Administrator by an owner or operator, or the review of such information by the Administrator, such time periods or deadlines may be changed by mutual agreement between the owner or operator and the Administrator. Procedures governing the implementation of this provision are specified in §63.9(i).

(b) *Initial applicability determination for this part.* (1) The provisions of this part apply to the owner or operator of any stationary source that—

(i) Emits or has the potential to emit any hazardous air pollutant listed in or pursuant to section 112(b) of the Act; and

(ii) Is subject to any standard, limitation, prohibition, or other federally enforceable requirement established pursuant to this part.

(2) [Reserved]

(3) An owner or operator of a stationary source who is in the relevant source category and who determines that the source is not subject to a relevant standard or other requirement established under this part must keep a record as specified in §63.10(b)(3).

(c) *Applicability of this part after a relevant standard has been set under this part.* (1) If a relevant standard has been established under this part, the owner or operator of an affected source must comply with the provisions of that standard and of this subpart as provided in paragraph (a)(4) of this section.

(2) Except as provided in §63.10(b)(3), if a relevant standard has been established under this part, the owner or operator of an affected source may be required to obtain a title V permit from a permitting authority in the State in which the source is located. Emission standards promulgated in this part for area sources pursuant to section 112(c)(3) of the Act will specify whether—

(i) States will have the option to exclude area sources affected by that standard from the requirement to obtain a title V permit (i.e., the standard will exempt the category of area sources altogether from the permitting requirement);

(ii) States will have the option to defer permitting of area sources in that category until the Administrator takes rulemaking action to determine applicability of the permitting requirements; or

(iii) If a standard fails to specify what the permitting requirements will be for area sources affected by such a standard, then area sources that are subject to the standard will be subject to the requirement to obtain a title V permit without any deferral.

(3)–(4) [Reserved]

(5) If an area source that otherwise would be subject to an emission standard or other requirement established under this part if it were a major source subsequently increases its emissions of hazardous air pollutants (or its potential to emit hazardous air pollutants) such that the source is a major source that is subject to the emission standard or other requirement, such source also shall be subject to the notification requirements of this subpart.

(d) [Reserved]

(e) If the Administrator promulgates an emission standard under section 112(d) or (h) of the Act that is applicable to a source subject to an emission limitation by permit established under section 112(j) of the Act, and the requirements under the section 112(j) emission limitation are substantially as effective as the promulgated emission standard, the owner or operator may request the permitting authority to revise the source's title V permit to reflect that the emission limitation in the permit satisfies the requirements of the promulgated emission standard. The process by which the permitting authority determines whether the section 112(j) emission limitation is substantially as effective as the promulgated emission standard must include, consistent with part 70 or 71 of this chapter, the opportunity for full public, EPA, and affected State review (including the opportunity for EPA's objection) prior to the permit revision being finalized. A negative determination by the permitting authority constitutes final action for purposes of review and appeal under the applicable title V operating permit program.

[59 FR 12430, Mar. 16, 1994, as amended at 67 FR 16595, Apr. 5, 2002]

§ 63.2 Definitions.

The terms used in this part are defined in the Act or in this section as follows:

Act means the Clean Air Act (42 U.S.C. 7401 *et seq* ., as amended by Pub. L. 101–549, 104 Stat. 2399).

Actual emissions is defined in subpart D of this part for the purpose of granting a compliance extension for an early reduction of hazardous air pollutants.

Administrator means the Administrator of the United States Environmental Protection Agency or his or her authorized representative (e.g., a State that has been delegated the authority to implement the provisions of this part).

Affected source, for the purposes of this part, means the collection of equipment, activities, or both within a single contiguous area and under common control that is included in a section 112(c) source category or subcategory for which a section 112(d) standard or other relevant standard is established pursuant to section 112 of the Act. Each relevant standard will define the "affected source," as defined in this paragraph unless a different definition is warranted based on a published justification as to why this definition would result in significant administrative, practical, or implementation problems and why the different definition would resolve those problems. The term "affected source," as used in this part, is separate and distinct from any other use of that term in EPA regulations such as those implementing title IV of the Act. Affected source may be defined differently for part 63 than affected facility and stationary source in parts 60 and 61, respectively. This definition of "affected source," and the procedures for adopting an alternative definition of "affected source," shall apply to each section 112(d) standard for which the initial proposed rule is signed by the Administrator after June 30, 2002.

Alternative emission limitation means conditions established pursuant to sections 112(i)(5) or 112(i)(6) of the Act by the Administrator or by a State with an approved permit program.

Alternative emission standard means an alternative means of emission limitation that, after notice and opportunity for public comment, has been demonstrated by an owner or operator to the Administrator's satisfaction to achieve a reduction in emissions of any air pollutant at least equivalent to the reduction in emissions of such pollutant achieved under a relevant design, equipment, work practice, or operational emission standard, or combination thereof, established under this part pursuant to section 112(h) of the Act.

Alternative test method means any method of sampling and analyzing for an air pollutant that is not a test method in this chapter and that has been demonstrated to the Administrator's satisfaction, using Method 301 in Appendix A of this part, to produce results adequate for the Administrator's determination that it may be used in place of a test method specified in this part.

Approved permit program means a State permit program approved by the Administrator as meeting the requirements of part 70 of this chapter or a Federal permit program established in this chapter pursuant to title V of the Act (42 U.S.C. 7661).

Area source means any stationary source of hazardous air pollutants that is not a major source as defined in this part.

Commenced means, with respect to construction or reconstruction of an affected source, that an owner or operator has undertaken a continuous program of construction or reconstruction or that an owner or operator has entered into a contractual obligation to undertake and complete, within a reasonable time, a continuous program of construction or reconstruction.

Compliance date means the date by which an affected source is required to be in compliance with a relevant standard, limitation, prohibition, or any federally enforceable requirement established by the Administrator (or a State with an approved permit program) pursuant to section 112 of the Act.

Compliance schedule means: (1) In the case of an affected source that is in compliance with all applicable requirements established under this part, a statement that the source will continue to comply with such requirements; or

(2) In the case of an affected source that is required to comply with applicable requirements by a future date, a statement that the source will meet such requirements on a timely basis and, if required by an applicable requirement, a detailed schedule of the dates by which each step toward compliance will be reached; or

(3) In the case of an affected source not in compliance with all applicable requirements established under this part, a schedule of remedial measures, including an enforceable sequence of actions or operations with milestones and a schedule for the submission of certified progress reports, where applicable, leading to compliance with a relevant standard, limitation, prohibition, or any federally enforceable requirement established pursuant to section 112 of the Act for which the affected source is not in compliance. This compliance schedule shall resemble and be at least as stringent as that contained in any judicial consent decree or administrative order to which the source is subject. Any such schedule of compliance shall be supplemental to, and shall not sanction noncompliance with, the applicable requirements on which it is based.

Construction means the on-site fabrication, erection, or installation of an affected source. Construction does not include the removal of all equipment comprising an affected source from an existing location and reinstallation of such equipment at a new location. The owner or operator of an existing affected source that is relocated may elect not to reinstall minor ancillary equipment including, but not limited to, piping, ductwork, and valves. However, removal and reinstallation of an affected source will be construed as reconstruction if it satisfies the criteria for reconstruction as defined in this section. The costs of replacing minor ancillary equipment must be considered in determining whether the existing affected source is reconstructed.

Continuous emission monitoring system (CEMS) means the total equipment that may be required to meet the data acquisition and availability requirements of this part, used to sample, condition (if applicable), analyze, and provide a record of emissions.

Continuous monitoring system (CMS) is a comprehensive term that may include, but is not limited to, continuous emission monitoring systems, continuous opacity monitoring systems, continuous parameter monitoring systems, or other manual or automatic monitoring that is used for demonstrating compliance with an applicable regulation on a continuous basis as defined by the regulation.

Continuous opacity monitoring system (COMS) means a continuous monitoring system that measures the opacity of emissions.

Continuous parameter monitoring system means the total equipment that may be required to meet the data acquisition and availability requirements of this part, used to sample, condition (if applicable), analyze, and provide a record of process or control system parameters.

Effective date means:

(1) With regard to an emission standard established under this part, the date of promulgation in theFederal Registerof such standard; or

(2) With regard to an alternative emission limitation or equivalent emission limitation determined by the Administrator (or a State with an approved permit program), the date that the alternative emission limitation or equivalent emission limitation becomes effective according to the provisions of this part.

Emission standard means a national standard, limitation, prohibition, or other regulation promulgated in a subpart of this part pursuant to sections 112(d), 112(h), or 112(f) of the Act.

Emissions averaging is a way to comply with the emission limitations specified in a relevant standard, whereby an affected source, if allowed under a subpart of this part, may create emission credits by reducing emissions from specific points to a level below that required by the relevant standard, and those credits are used to offset emissions from points that are not controlled to the level required by the relevant standard.

EPA means the United States Environmental Protection Agency.

Equivalent emission limitation means any maximum achievable control technology emission limitation or requirements which are applicable to a major source of hazardous air pollutants and are adopted by the Administrator (or a State with an approved permit program) on a case-by-case basis, pursuant to section 112(g) or (j) of the Act.

Excess emissions and continuous monitoring system performance report is a report that must be submitted periodically by an affected source in order to provide data on its compliance with relevant emission limits, operating parameters, and the performance of its continuous parameter monitoring systems.

Existing source means any affected source that is not a new source.

Federally enforceable means all limitations and conditions that are enforceable by the Administrator and citizens under the Act or that are enforceable under other statutes administered by the Administrator. Examples of federally enforceable limitations and conditions include, but are not limited to:

(1) Emission standards, alternative emission standards, alternative emission limitations, and equivalent emission limitations established pursuant to section 112 of the Act as amended in 1990;

(2) New source performance standards established pursuant to section 111 of the Act, and emission standards established pursuant to section 112 of the Act before it was amended in 1990;

(3) All terms and conditions in a title V permit, including any provisions that limit a source's potential to emit, unless expressly designated as not federally enforceable;

(4) Limitations and conditions that are part of an approved State Implementation Plan (SIP) or a Federal Implementation Plan (FIP);

(5) Limitations and conditions that are part of a Federal construction permit issued under 40 CFR 52.21 or any construction permit issued under regulations approved by the EPA in accordance with 40 CFR part 51;

(6) Limitations and conditions that are part of an operating permit where the permit and the permitting program pursuant to which it was issued meet all of the following criteria:

(i) The operating permit program has been submitted to and approved by EPA into a State implementation plan (SIP) under section 110 of the CAA;

(ii) The SIP imposes a legal obligation that operating permit holders adhere to the terms and limitations of such permits and provides that permits which do not conform to the operating permit program requirements and the requirements of EPA's underlying regulations may be deemed not "federally enforceable" by EPA;

(iii) The operating permit program requires that all emission limitations, controls, and other requirements imposed by such permits will be at least as stringent as any other applicable limitations and requirements contained in the SIP or enforceable under the SIP, and that the program may not issue permits that waive, or make less stringent, any limitations or requirements contained in or issued pursuant to the SIP, or that are otherwise "federally enforceable";

(iv) The limitations, controls, and requirements in the permit in question are permanent, quantifiable, and otherwise enforceable as a practical matter; and

(v) The permit in question was issued only after adequate and timely notice and opportunity for comment for EPA and the public.

(7) Limitations and conditions in a State rule or program that has been approved by the EPA under subpart E of this part for the purposes of implementing and enforcing section 112; and

(8) Individual consent agreements that the EPA has legal authority to create.

Fixed capital cost means the capital needed to provide all the depreciable components of an existing source.

Force majeure means, for purposes of §63.7, an event that will be or has been caused by circumstances beyond the control of the affected facility, its contractors, or any entity controlled by the affected facility that prevents the owner or operator from complying with the regulatory requirement to conduct performance tests within the specified timeframe despite the affected facility's best efforts to fulfill the obligation. Examples of such events are acts of nature, acts of war or terrorism, or equipment failure or safety hazard beyond the control of the affected facility.

Fugitive emissions means those emissions from a stationary source that could not reasonably pass through a stack, chimney, vent, or other functionally equivalent opening. Under section 112 of the Act, all fugitive emissions are to be considered in determining whether a stationary source is a major source.

Hazardous air pollutant means any air pollutant listed in or pursuant to section 112(b) of the Act.

Issuance of a part 70 permit will occur, if the State is the permitting authority, in accordance with the requirements of part 70 of this chapter and the applicable, approved State permit program. When the EPA is the permitting authority, issuance of a title V permit occurs immediately after the EPA takes final action on the final permit.

Major source means any stationary source or group of stationary sources located within a contiguous area and under common control that emits or has the potential to emit considering controls, in the aggregate, 10 tons per year or more of any hazardous air pollutant or 25 tons per year or more of any combination of hazardous air pollutants, unless the Administrator establishes a lesser quantity, or in the case of radionuclides, different criteria from those specified in this sentence.

Malfunction means any sudden, infrequent, and not reasonably preventable failure of air pollution control and monitoring equipment, process equipment, or a process to operate in a normal or usual manner which causes, or has the potential to cause, the emission limitations in an applicable standard to be exceeded. Failures that are caused in part by poor maintenance or careless operation are not malfunctions.

Monitoring means the collection and use of measurement data or other information to control the operation of a process or pollution control device or to verify a work practice standard relative to assuring compliance with applicable requirements. Monitoring is composed of four elements:

(1) Indicator(s) of performance—the parameter or parameters you measure or observe for demonstrating proper operation of the pollution control measures or compliance with the applicable emissions limitation or standard. Indicators of performance may include direct or predicted emissions measurements (including opacity), operational parametric values that correspond to process or control device (and capture system) efficiencies or emissions rates, and recorded findings of inspection of work practice activities, materials tracking, or design characteristics. Indicators may be expressed as a single maximum or minimum value, a

function of process variables (for example, within a range of pressure drops), a particular operational or work practice status (for example, a damper position, completion of a waste recovery task, materials tracking), or an interdependency between two or among more than two variables.

(2) Measurement techniques—the means by which you gather and record information of or about the indicators of performance. The components of the measurement technique include the detector type, location and installation specifications, inspection procedures, and quality assurance and quality control measures. Examples of measurement techniques include continuous emission monitoring systems, continuous opacity monitoring systems, continuous parametric monitoring systems, and manual inspections that include making records of process conditions or work practices.

(3) Monitoring frequency—the number of times you obtain and record monitoring data over a specified time interval. Examples of monitoring frequencies include at least four points equally spaced for each hour for continuous emissions or parametric monitoring systems, at least every 10 seconds for continuous opacity monitoring systems, and at least once per operating day (or week, month, etc.) for work practice or design inspections.

(4) Averaging time—the period over which you average and use data to verify proper operation of the pollution control approach or compliance with the emissions limitation or standard. Examples of averaging time include a 3-hour average in units of the emissions limitation, a 30-day rolling average emissions value, a daily average of a control device operational parametric range, and an instantaneous alarm.

New affected source means the collection of equipment, activities, or both within a single contiguous area and under common control that is included in a section 112(c) source category or subcategory that is subject to a section 112(d) or other relevant standard for new sources. This definition of "new affected source," and the criteria to be utilized in implementing it, shall apply to each section 112(d) standard for which the initial proposed rule is signed by the Administrator after June 30, 2002. Each relevant standard will define the term "new affected source," which will be the same as the "affected source" unless a different collection is warranted based on consideration of factors including:

(1) Emission reduction impacts of controlling individual sources versus groups of sources;

(2) Cost effectiveness of controlling individual equipment;

(3) Flexibility to accommodate common control strategies;

(4) Cost/benefits of emissions averaging;

(5) Incentives for pollution prevention;

(6) Feasibility and cost of controlling processes that share common equipment (e.g., product recovery devices);

(7) Feasibility and cost of monitoring; and

(8) Other relevant factors.

New source means any affected source the construction or reconstruction of which is commenced after the Administrator first proposes a relevant emission standard under this part establishing an emission standard applicable to such source.

One-hour period, unless otherwise defined in an applicable subpart, means any 60-minute period commencing on the hour.

Opacity means the degree to which emissions reduce the transmission of light and obscure the view of an object in the background. For continuous opacity monitoring systems, opacity means the fraction of incident light that is attenuated by an optical medium.

Owner or operator means any person who owns, leases, operates, controls, or supervises a stationary source.

Performance audit means a procedure to analyze blind samples, the content of which is known by the Administrator, simultaneously with the analysis of performance test samples in order to provide a measure of test data quality.

Performance evaluation means the conduct of relative accuracy testing, calibration error testing, and other measurements used in validating the continuous monitoring system data.

Performance test means the collection of data resulting from the execution of a test method (usually three emission test runs) used to demonstrate compliance with a relevant emission standard as specified in the performance test section of the relevant standard.

Permit modification means a change to a title V permit as defined in regulations codified in this chapter to implement title V of the Act (42 U.S.C. 7661).

Permit program means a comprehensive State operating permit system established pursuant to title V of the Act (42 U.S.C. 7661) and regulations codified in part 70 of this chapter and applicable State regulations, or a comprehensive Federal operating permit system established pursuant to title V of the Act and regulations codified in this chapter.

Permit revision means any permit modification or administrative permit amendment to a title V permit as defined in regulations codified in this chapter to implement title V of the Act (42 U.S.C. 7661).

Permitting authority means: (1) The State air pollution control agency, local agency, other State agency, or other agency authorized by the Administrator to carry out a permit program under part 70 of this chapter; or

(2) The Administrator, in the case of EPA-implemented permit programs under title V of the Act (42 U.S.C. 7661).

Pollution Prevention means *source reduction* as defined under the Pollution Prevention Act (42 U.S.C. 13101–13109). The definition is as follows:

(1) *Source reduction* is any practice that:

(i) Reduces the amount of any hazardous substance, pollutant, or contaminant entering any waste stream or otherwise released into the environment (including fugitive emissions) prior to recycling, treatment, or disposal; and

(ii) Reduces the hazards to public health and the environment associated with the release of such substances, pollutants, or contaminants.

(2) The term *source reduction* includes equipment or technology modifications, process or procedure modifications, reformulation or redesign of products, substitution of raw materials, and improvements in housekeeping, maintenance, training, or inventory control.

(3) The term *source reduction* does not include any practice that alters the physical, chemical, or biological characteristics or the volume of a hazardous substance, pollutant, or contaminant through a process or activity which itself is not integral to and necessary for the production of a product or the providing of a service.

Potential to emit means the maximum capacity of a stationary source to emit a pollutant under its physical and operational design. Any physical or operational limitation on the capacity of the stationary source to emit a pollutant, including air pollution control equipment and restrictions on hours of operation or on the type or amount of material combusted, stored, or processed, shall be treated as part of its design if the limitation or the effect it would have on emissions is federally enforceable.

Reconstruction, unless otherwise defined in a relevant standard, means the replacement of components of an affected or a previously nonaffected source to such an extent that:

(1) The fixed capital cost of the new components exceeds 50 percent of the fixed capital cost that would be required to construct a comparable new source; and

(2) It is technologically and economically feasible for the reconstructed source to meet the relevant standard(s) established by the Administrator (or a State) pursuant to section 112 of the Act. Upon reconstruction, an affected source, or a stationary source that becomes an affected source, is subject to relevant standards for new sources, including compliance dates, irrespective of any change in emissions of hazardous air pollutants from that source.

Regulation promulgation schedule means the schedule for the promulgation of emission standards under this part, established by the Administrator pursuant to section 112(e) of the Act and published in theFederal Register.

Relevant standard means:

(1) An emission standard;

(2) An alternative emission standard;

(3) An alternative emission limitation; or

(4) An equivalent emission limitation established pursuant to section 112 of the Act that applies to the collection of equipment, activities, or both regulated by such standard or limitation. A relevant standard may include or consist of a design, equipment, work practice, or operational requirement, or other measure, process, method, system, or technique (including prohibition of emissions) that the Administrator (or a State) establishes for new or existing sources to which such standard or limitation applies. Every relevant standard established pursuant to section 112 of the Act includes subpart A of this part, as provided by §63.1(a)(4), and all applicable appendices of this part or of other parts of this chapter that are referenced in that standard.

Responsible official means one of the following:

(1) For a corporation: A president, secretary, treasurer, or vice president of the corporation in charge of a principal business function, or any other person who performs similar policy or decision-making functions for the corporation, or a duly authorized representative of such person if the representative is responsible for the overall operation of one or more manufacturing, production, or operating facilities and either:

(i) The facilities employ more than 250 persons or have gross annual sales or expenditures exceeding $25 million (in second quarter 1980 dollars); or

(ii) The delegation of authority to such representative is approved in advance by the Administrator.

(2) For a partnership or sole proprietorship: a general partner or the proprietor, respectively.

(3) For a municipality, State, Federal, or other public agency: either a principal executive officer or ranking elected official. For the purposes of this part, a principal executive officer of a Federal agency includes the chief executive officer having responsibility for the overall operations of a principal geographic unit of the agency (e.g., a Regional Administrator of the EPA).

(4) For affected sources (as defined in this part) applying for or subject to a title V permit: "responsible official" shall have the same meaning as defined in part 70 or Federal title V regulations in this chapter (42 U.S.C. 7661), whichever is applicable.

Run means one of a series of emission or other measurements needed to determine emissions for a representative operating period or cycle as specified in this part.

Shutdown means the cessation of operation of an affected source or portion of an affected source for any purpose.

Six-minute period means, with respect to opacity determinations, any one of the 10 equal parts of a 1-hour period.

Source at a Performance Track member facility means a major or area source located at a facility which has been accepted by EPA for membership in the Performance Track Program (as described at *www.epa.gov/PerformanceTrack*) and is still a member of the Program. The Performance Track Program is a voluntary program that encourages continuous environmental improvement through the use of environmental management systems, local community outreach, and measurable results.

Standard conditions means a temperature of 293 K (68 °F) and a pressure of 101.3 kilopascals (29.92 in. Hg).

Startup means the setting in operation of an affected source or portion of an affected source for any purpose.

State means all non-Federal authorities, including local agencies, interstate associations, and State-wide programs, that have delegated authority to implement: (1) The provisions of this part and/or (2) the permit program established under part 70 of this chapter. The term State shall have its conventional meaning where clear from the context.

Stationary source means any building, structure, facility, or installation which emits or may emit any air pollutant.

Test method means the validated procedure for sampling, preparing, and analyzing for an air pollutant specified in a relevant standard as the performance test procedure. The test method may include methods described in an appendix of this chapter, test methods incorporated by reference in this part, or methods validated for an application through procedures in Method 301 of appendix A of this part.

Title V permit means any permit issued, renewed, or revised pursuant to Federal or State regulations established to implement title V of the Act (42 U.S.C. 7661). A title V permit issued by a State permitting authority is called a part 70 permit in this part.

Visible emission means the observation of an emission of opacity or optical density above the threshold of vision.

Working day means any day on which Federal Government offices (or State government offices for a State that has obtained delegation under section 112(l)) are open for normal business. Saturdays, Sundays, and official Federal (or where delegated, State) holidays are not working days.

[59 FR 12430, Mar. 16, 1994, as amended at 67 FR 16596, Apr. 5, 2002; 68 FR 32600, May 30, 2003; 69 FR 21752, Apr. 22, 2004; 72 FR 27443, May 16, 2007]

§ 63.3 Units and abbreviations.

Used in this part are abbreviations and symbols of units of measure. These are defined as follows:

(a) *System International (SI) units of measure:*

A = ampere

g = gram

Hz = hertz

J = joule

°K = degree Kelvin

kg = kilogram

l = liter

m = meter

m^3 = cubic meter

mg = milligram = 10^{-3}gram

ml = milliliter = 10^{-3}liter

mm = millimeter = 10^{-3}meter

Mg = megagram = 10^6 gram = metric ton

MJ = megajoule

mol = mole

N = newton

ng = nanogram = 10^{-9}gram

nm = nanometer = 10^{-9}meter

Pa = pascal

s = second

V = volt

W = watt

Ω = ohm

μg = microgram = 10^{-6}gram

μl = microliter = 10^{-6}liter

(b) *Other units of measure:*

Btu = British thermal unit

°C = degree Celsius (centigrade)

cal = calorie

cfm = cubic feet per minute

cc = cubic centimeter

cu ft = cubic feet

d = day

dcf = dry cubic feet

dcm = dry cubic meter

dscf = dry cubic feet at standard conditions

dscm = dry cubic meter at standard conditions

eq = equivalent

°F degree Fahrenheit

ft = feet

ft^2 = square feet

ft^3 = cubic feet

gal = gallon

gr = grain

g-eq = gram equivalent

g-mole = gram mole

hr = hour

in. = inch

in. H_2O = inches of water

K = 1,000

kcal = kilocalorie

lb = pound

lpm = liter per minute

meq = milliequivalent

min = minute

MW = molecular weight

oz = ounces

ppb = parts per billion

ppbw = parts per billion by weight

ppbv = parts per billion by volume

ppm = parts per million

ppmw = parts per million by weight

ppmv = parts per million by volume

psia = pounds per square inch absolute

psig = pounds per square inch gage

°R = degree Rankine

scf = cubic feet at standard conditions

scfh = cubic feet at standard conditions per hour

scm = cubic meter at standard conditions

scmm = cubic meter at standard conditions per minute

sec = second

sq ft = square feet

std = at standard conditions

v/v = volume per volume

yd^2 = square yards

yr = year

(c) *Miscellaneous:*

act = actual

avg = average

I.D. = inside diameter

M = molar

N = normal

O.D. = outside diameter

% = percent

[59 FR 12430, Mar. 16, 1994, as amended at 67 FR 16598, Apr. 5, 2002]

§ 63.4 Prohibited activities and circumvention.

(a) *Prohibited activities.* (1) No owner or operator subject to the provisions of this part must operate any affected source in violation of the requirements of this part. Affected sources subject to and in compliance with either an extension of compliance or an exemption from compliance are not in violation of the requirements of this part. An extension of compliance can be granted by the Administrator under this part; by a State with an approved permit program; or by the President under section 112(i)(4) of the Act.

(2) No owner or operator subject to the provisions of this part shall fail to keep records, notify, report, or revise reports as required under this part.

(3)–(5) [Reserved]

(b) *Circumvention.* No owner or operator subject to the provisions of this part shall build, erect, install, or use any article, machine, equipment, or process to conceal an emission that would otherwise constitute noncompliance with a relevant standard. Such concealment includes, but is not limited to—

(1) The use of diluents to achieve compliance with a relevant standard based on the concentration of a pollutant in the effluent discharged to the atmosphere;

(2) The use of gaseous diluents to achieve compliance with a relevant standard for visible emissions; and

(c) *Fragmentation.* Fragmentation after November 15, 1990 which divides ownership of an operation, within the same facility among various owners where there is no real change in control, will not affect applicability. The owner and operator must not use fragmentation or phasing of reconstruction activities (i.e., intentionally dividing reconstruction into multiple parts for purposes of avoiding new source requirements) to avoid becoming subject to new source requirements.

[59 FR 12430, Mar. 16, 1994, as amended at 67 FR 16598, Apr. 5, 2002]

§ 63.5 Preconstruction review and notification requirements.

(a) *Applicability.* (1) This section implements the preconstruction review requirements of section 112(i)(1). After the effective date of a relevant standard, promulgated pursuant to section 112(d), (f), or (h) of the Act, under this part, the preconstruction review requirements in this section apply to the owner or operator of new affected sources and reconstructed affected sources that are major-emitting as specified in this section. New and reconstructed affected sources that commence construction or reconstruction before the effective date of a relevant standard are not subject to the preconstruction review requirements specified in paragraphs (b)(3), (d), and (e) of this section.

(2) This section includes notification requirements for new affected sources and reconstructed affected sources that are not major-emitting affected sources and that are or become subject to a relevant promulgated emission standard after the effective date of a relevant standard promulgated under this part.

(b) *Requirements for existing, newly constructed, and reconstructed sources.* (1) A new affected source for which construction commences after proposal of a relevant standard is subject to relevant standards for new affected sources, including compliance dates. An affected source for which reconstruction commences after proposal of a relevant standard is subject to relevant standards for new sources, including compliance dates, irrespective of any change in emissions of hazardous air pollutants from that source.

(2) [Reserved]

(3) After the effective date of any relevant standard promulgated by the Administrator under this part, no person may, without obtaining written approval in advance from the Administrator in accordance with the procedures specified in paragraphs (d) and (e) of this section, do any of the following:

(i) Construct a new affected source that is major-emitting and subject to such standard;

(ii) Reconstruct an affected source that is major-emitting and subject to such standard; or

(iii) Reconstruct a major source such that the source becomes an affected source that is major-emitting and subject to the standard.

(4) After the effective date of any relevant standard promulgated by the Administrator under this part, an owner or operator who constructs a new affected source that is not major-emitting or reconstructs an affected source that is not major-emitting that is subject to such standard, or reconstructs a source such that the source becomes an affected source subject to the standard, must notify the Administrator of the intended construction or reconstruction. The notification must be submitted in accordance with the procedures in §63.9(b).

(5) [Reserved]

(6) After the effective date of any relevant standard promulgated by the Administrator under this part, equipment added (or a process change) to an affected source that is within the scope of the definition of affected source under the relevant standard must be considered part of the affected source and subject to all provisions of the relevant standard established for that affected source.

(c) [Reserved]

(d) *Application for approval of construction or reconstruction.* The provisions of this paragraph implement section 112(i)(1) of the Act.

(1) *General application requirements.* (i) An owner or operator who is subject to the requirements of paragraph (b)(3) of this section must submit to the Administrator an application for approval of the construction or reconstruction. The application must be submitted as soon as practicable before actual construction or reconstruction begins. The application for approval of construction or reconstruction may be used to fulfill the initial notification requirements of §63.9(b)(5). The owner or operator may submit the application for approval well in advance of the date actual construction or reconstruction begins in order to ensure a timely review by the Administrator and that the planned date to begin will not be delayed.

(ii) A separate application shall be submitted for each construction or reconstruction. Each application for approval of construction or reconstruction shall include at a minimum:

(A) The applicant's name and address;

(B) A notification of intention to construct a new major affected source or make any physical or operational change to a major affected source that may meet or has been determined to meet the criteria for a reconstruction, as defined in §63.2 or in the relevant standard;

(C) The address (i.e., physical location) or proposed address of the source;

(D) An identification of the relevant standard that is the basis of the application;

(E) The expected date of the beginning of actual construction or reconstruction;

(F) The expected completion date of the construction or reconstruction;

(G) [Reserved]

(H) The type and quantity of hazardous air pollutants emitted by the source, reported in units and averaging times and in accordance with the test methods specified in the relevant standard, or if actual emissions data are not yet available, an estimate of the type and quantity of hazardous air pollutants expected to be emitted by the source reported in units and averaging times specified in the relevant standard. The owner or operator may submit percent reduction information if a relevant standard is established in terms of percent reduction. However, operating parameters, such as flow rate, shall be included in the submission to the extent that they demonstrate performance and compliance; and

(I) [Reserved]

(J) Other information as specified in paragraphs (d)(2) and (d)(3) of this section.

(iii) An owner or operator who submits estimates or preliminary information in place of the actual emissions data and analysis required in paragraphs (d)(1)(ii)(H) and (d)(2) of this section shall submit the actual, measured emissions data and other correct information as soon as available but no later than with the notification of compliance status required in §63.9(h) (see §63.9(h)(5)).

(2) *Application for approval of construction.* Each application for approval of construction must include, in addition to the information required in paragraph (d)(1)(ii) of this section, technical information describing the proposed nature, size, design, operating design capacity, and method of operation of the source, including an identification of each type of emission point for each type of hazardous air pollutant that is emitted (or could reasonably be anticipated to be emitted) and a description of the planned air pollution control system (equipment or method) for each emission point. The description of the equipment to be used for the control of emissions must include each control device for each hazardous air pollutant and the estimated control efficiency (percent) for each control device. The description of the method to be used for the control of emissions must include an estimated control efficiency (percent) for that method. Such technical information must include calculations of emission estimates in sufficient detail to permit assessment of the validity of the calculations.

(3) *Application for approval of reconstruction.* Each application for approval of reconstruction shall include, in addition to the information required in paragraph (d)(1)(ii) of this section—

(i) A brief description of the affected source and the components that are to be replaced;

(ii) A description of present and proposed emission control systems (i.e., equipment or methods). The description of the equipment to be used for the control of emissions shall include each control device for each hazardous air pollutant and the estimated control efficiency (percent) for each control device. The description of the method to be used for the control of emissions shall include an estimated control efficiency (percent) for that method. Such technical information shall include calculations of emission estimates in sufficient detail to permit assessment of the validity of the calculations;

(iii) An estimate of the fixed capital cost of the replacements and of constructing a comparable entirely new source;

(iv) The estimated life of the affected source after the replacements; and

(v) A discussion of any economic or technical limitations the source may have in complying with relevant standards or other requirements after the proposed replacements. The discussion shall be sufficiently detailed to demonstrate to the Administrator's satisfaction that the technical or economic limitations affect the source's ability to comply with the relevant standard and how they do so.

(vi) If in the application for approval of reconstruction the owner or operator designates the affected source as a reconstructed source and declares that there are no economic or technical limitations to prevent the source from complying with all relevant standards or other requirements, the owner or operator need not submit the information required in paragraphs (d)(3)(iii) through (d)(3)(v) of this section.

(4) *Additional information.* The Administrator may request additional relevant information after the submittal of an application for approval of construction or reconstruction.

(e) *Approval of construction or reconstruction.* (1)(i) If the Administrator determines that, if properly constructed, or reconstructed, and operated, a new or existing source for which an application under paragraph (d) of this section was submitted will not cause emissions in violation of the relevant standard(s) and any other federally enforceable requirements, the Administrator will approve the construction or reconstruction.

(ii) In addition, in the case of reconstruction, the Administrator's determination under this paragraph will be based on:

(A) The fixed capital cost of the replacements in comparison to the fixed capital cost that would be required to construct a comparable entirely new source;

(B) The estimated life of the source after the replacements compared to the life of a comparable entirely new source;

(C) The extent to which the components being replaced cause or contribute to the emissions from the source; and

(D) Any economic or technical limitations on compliance with relevant standards that are inherent in the proposed replacements.

(2)(i) The Administrator will notify the owner or operator in writing of approval or intention to deny approval of construction or reconstruction within 60 calendar days after receipt of sufficient information to evaluate an application submitted under paragraph (d) of this section. The 60-day approval or denial period will begin after the owner or operator has been notified in writing that his/her application is complete. The Administrator will notify the owner or operator in writing of the status of his/her application, that is, whether the application contains sufficient information to make a determination, within 30 calendar days after receipt of the original application and within 30 calendar days after receipt of any supplementary information that is submitted.

(ii) When notifying the owner or operator that his/her application is not complete, the Administrator will specify the information needed to complete the application and provide notice of opportunity for the applicant to present, in writing, within 30 calendar days after he/she is notified of the incomplete application, additional information or arguments to the Administrator to enable further action on the application.

(3) Before denying any application for approval of construction or reconstruction, the Administrator will notify the applicant of the Administrator's intention to issue the denial together with—

(i) Notice of the information and findings on which the intended denial is based; and

(ii) Notice of opportunity for the applicant to present, in writing, within 30 calendar days after he/she is notified of the intended denial, additional information or arguments to the Administrator to enable further action on the application.

(4) A final determination to deny any application for approval will be in writing and will specify the grounds on which the denial is based. The final determination will be made within 60 calendar days of presentation of additional information or arguments (if the application is complete), or within 60 calendar days after the final date specified for presentation if no presentation is made.

(5) Neither the submission of an application for approval nor the Administrator's approval of construction or reconstruction shall—

(i) Relieve an owner or operator of legal responsibility for compliance with any applicable provisions of this part or with any other applicable Federal, State, or local requirement; or

(ii) Prevent the Administrator from implementing or enforcing this part or taking any other action under the Act.

(f) *Approval of construction or reconstruction based on prior State preconstruction review.* (1) Preconstruction review procedures that a State utilizes for other purposes may also be utilized for purposes of this section if the procedures are substantially equivalent to those specified in this section. The Administrator will approve an application for construction or reconstruction specified in paragraphs (b)(3) and (d) of this section if the owner or operator of a new affected source or reconstructed affected source, who is subject to such requirement meets the following conditions:

(i) The owner or operator of the new affected source or reconstructed affected source has undergone a preconstruction review and approval process in the State in which the source is (or would be) located and has received a federally enforceable construction permit that contains a finding that the source will meet the relevant promulgated emission standard, if the source is properly built and operated.

(ii) Provide a statement from the State or other evidence (such as State regulations) that it considered the factors specified in paragraph (e)(1) of this section.

(2) The owner or operator must submit to the Administrator the request for approval of construction or reconstruction under this paragraph (f)(2) no later than the application deadline specified in paragraph (d)(1) of this section (see also §63.9(b)(2)). The owner or operator must include in the request information sufficient for the Administrator's determination. The Administrator will evaluate the owner or operator's request in accordance with the procedures specified in paragraph (e) of this section. The Administrator may request additional relevant information after the submittal of a request for approval of construction or reconstruction under this paragraph (f)(2).

[59 FR 12430, Mar. 16, 1994, as amended at 67 FR 16598, Apr. 5, 2002]

§ 63.6 Compliance with standards and maintenance requirements.

(a) *Applicability.* (1) The requirements in this section apply to the owner or operator of affected sources for which any relevant standard has been established pursuant to section 112 of the Act and the applicability of such requirements is set out in accordance with §63.1(a)(4) unless—

(i) The Administrator (or a State with an approved permit program) has granted an extension of compliance consistent with paragraph (i) of this section; or

(ii) The President has granted an exemption from compliance with any relevant standard in accordance with section 112(i)(4) of the Act.

(2) If an area source that otherwise would be subject to an emission standard or other requirement established under this part if it were a major source subsequently increases its emissions of hazardous air

pollutants (or its potential to emit hazardous air pollutants) such that the source is a major source, such source shall be subject to the relevant emission standard or other requirement.

(b) *Compliance dates for new and reconstructed sources.* (1) Except as specified in paragraphs (b)(3) and (4) of this section, the owner or operator of a new or reconstructed affected source for which construction or reconstruction commences after proposal of a relevant standard that has an initial startup before the effective date of a relevant standard established under this part pursuant to section 112(d), (f), or (h) of the Act must comply with such standard not later than the standard's effective date.

(2) Except as specified in paragraphs (b)(3) and (4) of this section, the owner or operator of a new or reconstructed affected source that has an initial startup after the effective date of a relevant standard established under this part pursuant to section 112(d), (f), or (h) of the Act must comply with such standard upon startup of the source.

(3) The owner or operator of an affected source for which construction or reconstruction is commenced after the proposal date of a relevant standard established under this part pursuant to section 112(d), 112(f), or 112(h) of the Act but before the effective date (that is, promulgation) of such standard shall comply with the relevant emission standard not later than the date 3 years after the effective date if:

(i) The promulgated standard (that is, the relevant standard) is more stringent than the proposed standard; for purposes of this paragraph, a finding that controls or compliance methods are "more stringent" must include control technologies or performance criteria and compliance or compliance assurance methods that are different but are substantially equivalent to those required by the promulgated rule, as determined by the Administrator (or his or her authorized representative); and

(ii) The owner or operator complies with the standard as proposed during the 3-year period immediately after the effective date.

(4) The owner or operator of an affected source for which construction or reconstruction is commenced after the proposal date of a relevant standard established pursuant to section 112(d) of the Act but before the proposal date of a relevant standard established pursuant to section 112(f) shall not be required to comply with the section 112(f) emission standard until the date 10 years after the date construction or reconstruction is commenced, except that, if the section 112(f) standard is promulgated more than 10 years after construction or reconstruction is commenced, the owner or operator must comply with the standard as provided in paragraphs (b)(1) and (2) of this section.

(5) The owner or operator of a new source that is subject to the compliance requirements of paragraph (b)(3) or (4) of this section must notify the Administrator in accordance with §63.9(d)

(6) [Reserved]

(7) When an area source becomes a major source by the addition of equipment or operations that meet the definition of new affected source in the relevant standard, the portion of the existing facility that is a new affected source must comply with all requirements of that standard applicable to new sources. The source owner or operator must comply with the relevant standard upon startup.

(c) *Compliance dates for existing sources.* (1) After the effective date of a relevant standard established under this part pursuant to section 112(d) or 112(h) of the Act, the owner or operator of an existing source shall comply with such standard by the compliance date established by the Administrator in the applicable subpart(s) of this part. Except as otherwise provided for in section 112 of the Act, in no case will the compliance date established for an existing source in an applicable subpart of this part exceed 3 years after the effective date of such standard.

(2) If an existing source is subject to a standard established under this part pursuant to section 112(f) of the Act, the owner or operator must comply with the standard by the date 90 days after the standard's effective date, or by the date specified in an extension granted to the source by the Administrator under paragraph (i)(4)(ii) of this section, whichever is later.

(3)–(4) [Reserved]

(5) Except as provided in paragraph (b)(7) of this section, the owner or operator of an area source that increases its emissions of (or its potential to emit) hazardous air pollutants such that the source becomes a major source shall be subject to relevant standards for existing sources. Such sources must comply by the date specified in the standards for existing area sources that become major sources. If no such compliance date is specified in the standards, the source shall have a period of time to comply with the relevant emission standard that is equivalent to the compliance period specified in the relevant standard for existing sources in existence at the time the standard becomes effective.

(d) [Reserved]

(e) *Operation and maintenance requirements.* (1)(i) At all times, including periods of startup, shutdown, and malfunction, the owner or operator must operate and maintain any affected source, including associated air pollution control equipment and monitoring equipment, in a manner consistent with safety and good air pollution control practices for minimizing emissions. During a period of startup, shutdown, or malfunction, this general duty to minimize emissions requires that the owner or operator reduce emissions from the affected source to the greatest extent which is consistent with safety and good air pollution control practices. The general duty to minimize emissions during a period of startup, shutdown, or malfunction does not require the owner or operator to achieve emission levels that would be required by the applicable standard at other times if this is not consistent with safety and good air pollution control practices, nor does it require the owner or operator to make any further efforts to reduce emissions if levels required by the applicable standard have been achieved. Determination of whether such operation and maintenance procedures are being used will be based on information available to the Administrator which may include, but is not limited to, monitoring results, review of operation and maintenance procedures (including the startup, shutdown, and malfunction plan required in paragraph (e)(3) of this section), review of operation and maintenance records, and inspection of the source.

(ii) Malfunctions must be corrected as soon as practicable after their occurrence. To the extent that an unexpected event arises during a startup, shutdown, or malfunction, an owner or operator must comply by minimizing emissions during such a startup, shutdown, and malfunction event consistent with safety and good air pollution control practices.

(iii) Operation and maintenance requirements established pursuant to section 112 of the Act are enforceable independent of emissions limitations or other requirements in relevant standards.

(2) [Reserved]

(3) *Startup, shutdown, and malfunction plan.* (i) The owner or operator of an affected source must develop a written startup, shutdown, and malfunction plan that describes, in detail, procedures for operating and maintaining the source during periods of startup, shutdown, and malfunction; and a program of corrective action for malfunctioning process, air pollution control, and monitoring equipment used to comply with the relevant standard. The startup, shutdown, and malfunction plan does not need to address any scenario that would not cause the source to exceed an applicable emission limitation in the relevant standard. This plan must be developed by the owner or operator by the source's compliance date for that relevant standard. The purpose of the startup, shutdown, and malfunction plan is to—

(A) Ensure that, at all times, the owner or operator operates and maintains each affected source, including associated air pollution control and monitoring equipment, in a manner which satisfies the general duty to minimize emissions established by paragraph (e)(1)(i) of this section;

(B) Ensure that owners or operators are prepared to correct malfunctions as soon as practicable after their occurrence in order to minimize excess emissions of hazardous air pollutants; and

(C) Reduce the reporting burden associated with periods of startup, shutdown, and malfunction (including corrective action taken to restore malfunctioning process and air pollution control equipment to its normal or usual manner of operation).

(ii) [Reserved]

(iii) When actions taken by the owner or operator during a startup or shutdown (and the startup or shutdown causes the source to exceed any applicable emission limitation in the relevant emission standards), or malfunction (including actions taken to correct a malfunction) are consistent with the procedures specified in the affected source's startup, shutdown, and malfunction plan, the owner or operator must keep records for that event which demonstrate that the procedures specified in the plan were followed. These records may take the form of a "checklist," or other effective form of recordkeeping that confirms conformance with the startup, shutdown, and malfunction plan and describes the actions taken for that event. In addition, the owner or operator must keep records of these events as specified in paragraph 63.10(b), including records of the occurrence and duration of each startup or shutdown (if the startup or shutdown causes the source to exceed any applicable emission limitation in the relevant emission standards), or malfunction of operation and each malfunction of the air pollution control and monitoring equipment. Furthermore, the owner or operator shall confirm that actions taken during the relevant reporting period during periods of startup, shutdown, and malfunction were consistent with the affected source's startup, shutdown and malfunction plan in the semiannual (or more frequent) startup, shutdown, and malfunction report required in §63.10(d)(5).

(iv) If an action taken by the owner or operator during a startup, shutdown, or malfunction (including an action taken to correct a malfunction) is not consistent with the procedures specified in the affected source's startup, shutdown, and malfunction plan, and the source exceeds any applicable emission limitation in the relevant emission standard, then the owner or operator must record the actions taken for that event and must report such actions within 2 working days after commencing actions inconsistent with the plan, followed by a letter within 7 working days after the end of the event, in accordance with §63.10(d)(5) (unless the owner or operator makes alternative reporting arrangements, in advance, with the Administrator).

(v) The owner or operator must maintain at the affected source a current startup, shutdown, and malfunction plan and must make the plan available upon request for inspection and copying by the Administrator. In addition, if the startup, shutdown, and malfunction plan is subsequently revised as provided in paragraph (e)(3)(viii) of this section, the owner or operator must maintain at the affected source each previous (i.e., superseded) version of the startup, shutdown, and malfunction plan, and must make each such previous version available for inspection and copying by the Administrator for a period of 5 years after revision of the plan. If at any time after adoption of a startup, shutdown, and malfunction plan the affected source ceases operation or is otherwise no longer subject to the provisions of this part, the owner or operator must retain a copy of the most recent plan for 5 years from the date the source ceases operation or is no longer subject to this part and must make the plan available upon request for inspection and copying by the Administrator. The Administrator may at any time request in writing that the owner or operator submit a copy of any startup, shutdown, and malfunction plan (or a portion thereof) which is maintained at the affected source or in the possession of the owner or operator. Upon receipt of such a request, the owner or operator must promptly submit a copy of the requested plan (or a portion thereof) to the Administrator. The owner or operator may elect to submit the required copy of any startup, shutdown, and malfunction plan to the Administrator in an electronic format. If the owner or operator claims that any portion of such a startup, shutdown, and malfunction plan is confidential business information entitled to protection from disclosure under section 114(c) of the Act or 40 CFR 2.301, the material which is claimed as confidential must be clearly designated in the submission.

(vi) To satisfy the requirements of this section to develop a startup, shutdown, and malfunction plan, the owner or operator may use the affected source's standard operating procedures (SOP) manual, or an Occupational Safety and Health Administration (OSHA) or other plan, provided the alternative plans meet all the requirements of this section and are made available for inspection or submitted when requested by the Administrator.

(vii) Based on the results of a determination made under paragraph (e)(1)(i) of this section, the Administrator may require that an owner or operator of an affected source make changes to the startup, shutdown, and malfunction plan for that source. The Administrator must require appropriate revisions to a startup, shutdown, and malfunction plan, if the Administrator finds that the plan:

(A) Does not address a startup, shutdown, or malfunction event that has occurred;

(B) Fails to provide for the operation of the source (including associated air pollution control and monitoring equipment) during a startup, shutdown, or malfunction event in a manner consistent with the general duty to minimize emissions established by paragraph (e)(1)(i) of this section;

(C) Does not provide adequate procedures for correcting malfunctioning process and/or air pollution control and monitoring equipment as quickly as practicable; or

(D) Includes an event that does not meet the definition of startup, shutdown, or malfunction listed in §63.2.

(viii) The owner or operator may periodically revise the startup, shutdown, and malfunction plan for the affected source as necessary to satisfy the requirements of this part or to reflect changes in equipment or procedures at the affected source. Unless the permitting authority provides otherwise, the owner or operator may make such revisions to the startup, shutdown, and malfunction plan without prior approval by the Administrator or the permitting authority. However, each such revision to a startup, shutdown, and malfunction plan must be reported in the semiannual report required by §63.10(d)(5). If the startup, shutdown, and malfunction plan fails to address or inadequately addresses an event that meets the characteristics of a malfunction but was not included in the startup, shutdown, and malfunction plan at the time the owner or operator developed the plan, the owner or operator must revise the startup, shutdown, and malfunction plan within 45 days after the event to include detailed procedures for operating and maintaining the source during similar malfunction events and a program of corrective action for similar malfunctions of process or air pollution control and monitoring equipment. In the event that the owner or operator makes any revision to the startup, shutdown, and malfunction plan which alters the scope of the activities at the source which are deemed to be a startup, shutdown, or malfunction, or otherwise modifies the applicability of any emission limit, work practice requirement, or other requirement in a standard established under this part, the revised plan shall not take effect until after the owner or operator has provided a written notice describing the revision to the permitting authority.

(ix) The title V permit for an affected source must require that the owner or operator develop a startup, shutdown, and malfunction plan which conforms to the provisions of this part, but may do so by citing to the relevant subpart or subparagraphs of paragraph (e) of this section. However, any revisions made to the startup, shutdown, and malfunction plan in accordance with the procedures established by this part shall not be deemed to constitute permit revisions under part 70 or part 71 of this chapter and the elements of the startup, shutdown, and malfunction plan shall not be considered an applicable requirement as defined in §70.2 and §71.2 of this chapter. Moreover, none of the procedures specified by the startup, shutdown, and malfunction plan for an affected source shall be deemed to fall within the permit shield provision in section 504(f) of the Act.

(f) *Compliance with nonopacity emission standards* —(1) *Applicability.* The non-opacity emission standards set forth in this part shall apply at all times except during periods of startup, shutdown, and malfunction, and as otherwise specified in an applicable subpart. If a startup, shutdown, or malfunction of one portion of an affected source does not affect the ability of particular emission points within other portions of the affected source to comply with the non-opacity emission standards set forth in this part, then that emission point must still be required to comply with the non-opacity emission standards and other applicable requirements.

(2) *Methods for determining compliance.* (i) The Administrator will determine compliance with nonopacity emission standards in this part based on the results of performance tests conducted according to the procedures in §63.7, unless otherwise specified in an applicable subpart of this part.

(ii) The Administrator will determine compliance with nonopacity emission standards in this part by evaluation of an owner or operator's conformance with operation and maintenance requirements, including the evaluation of monitoring data, as specified in §63.6(e) and applicable subparts of this part.

(iii) If an affected source conducts performance testing at startup to obtain an operating permit in the State in which the source is located, the results of such testing may be used to demonstrate compliance with a relevant standard if—

(A) The performance test was conducted within a reasonable amount of time before an initial performance test is required to be conducted under the relevant standard;

(B) The performance test was conducted under representative operating conditions for the source;

(C) The performance test was conducted and the resulting data were reduced using EPA-approved test methods and procedures, as specified in §63.7(e) of this subpart; and

(D) The performance test was appropriately quality-assured, as specified in §63.7(c).

(iv) The Administrator will determine compliance with design, equipment, work practice, or operational emission standards in this part by review of records, inspection of the source, and other procedures specified in applicable subparts of this part.

(v) The Administrator will determine compliance with design, equipment, work practice, or operational emission standards in this part by evaluation of an owner or operator's conformance with operation and maintenance requirements, as specified in paragraph (e) of this section and applicable subparts of this part.

(3) *Finding of compliance*. The Administrator will make a finding concerning an affected source's compliance with a non-opacity emission standard, as specified in paragraphs (f)(1) and (2) of this section, upon obtaining all the compliance information required by the relevant standard (including the written reports of performance test results, monitoring results, and other information, if applicable), and information available to the Administrator pursuant to paragraph (e)(1)(i) of this section.

(g) *Use of an alternative nonopacity emission standard.* (1) If, in the Administrator's judgment, an owner or operator of an affected source has established that an alternative means of emission limitation will achieve a reduction in emissions of a hazardous air pollutant from an affected source at least equivalent to the reduction in emissions of that pollutant from that source achieved under any design, equipment, work practice, or operational emission standard, or combination thereof, established under this part pursuant to section 112(h) of the Act, the Administrator will publish in theFederal Registera notice permitting the use of the alternative emission standard for purposes of compliance with the promulgated standard. AnyFederal Registernotice under this paragraph shall be published only after the public is notified and given the opportunity to comment. Such notice will restrict the permission to the stationary source(s) or category(ies) of sources from which the alternative emission standard will achieve equivalent emission reductions. The Administrator will condition permission in such notice on requirements to assure the proper operation and maintenance of equipment and practices required for compliance with the alternative emission standard and other requirements, including appropriate quality assurance and quality control requirements, that are deemed necessary.

(2) An owner or operator requesting permission under this paragraph shall, unless otherwise specified in an applicable subpart, submit a proposed test plan or the results of testing and monitoring in accordance with §63.7 and §63.8, a description of the procedures followed in testing or monitoring, and a description of pertinent conditions during testing or monitoring. Any testing or monitoring conducted to request permission to use an alternative nonopacity emission standard shall be appropriately quality assured and quality controlled, as specified in §63.7 and §63.8.

(3) The Administrator may establish general procedures in an applicable subpart that accomplish the requirements of paragraphs (g)(1) and (g)(2) of this section.

(h) *Compliance with opacity and visible emission standards* —(1) *Applicability.* The opacity and visible emission standards set forth in this part must apply at all times except during periods of startup, shutdown, and malfunction, and as otherwise specified in an applicable subpart. If a startup, shutdown, or malfunction of one portion of an affected source does not affect the ability of particular emission points within other portions of the affected source to comply with the opacity and visible emission standards set forth in this part, then that emission point shall still be required to comply with the opacity and visible emission standards and other applicable requirements.

(2) *Methods for determining compliance.* (i) The Administrator will determine compliance with opacity and visible emission standards in this part based on the results of the test method specified in an applicable subpart. Whenever a continuous opacity monitoring system (COMS) is required to be installed to determine compliance with numerical opacity emission standards in this part, compliance with opacity emission standards in this part shall be determined by using the results from the COMS. Whenever an opacity

emission test method is not specified, compliance with opacity emission standards in this part shall be determined by conducting observations in accordance with Test Method 9 in appendix A of part 60 of this chapter or the method specified in paragraph (h)(7)(ii) of this section. Whenever a visible emission test method is not specified, compliance with visible emission standards in this part shall be determined by conducting observations in accordance with Test Method 22 in appendix A of part 60 of this chapter.

(ii) [Reserved]

(iii) If an affected source undergoes opacity or visible emission testing at startup to obtain an operating permit in the State in which the source is located, the results of such testing may be used to demonstrate compliance with a relevant standard if—

(A) The opacity or visible emission test was conducted within a reasonable amount of time before a performance test is required to be conducted under the relevant standard;

(B) The opacity or visible emission test was conducted under representative operating conditions for the source;

(C) The opacity or visible emission test was conducted and the resulting data were reduced using EPA-approved test methods and procedures, as specified in §63.7(e); and

(D) The opacity or visible emission test was appropriately quality-assured, as specified in §63.7(c) of this section.

(3) [Reserved]

(4) *Notification of opacity or visible emission observations.* The owner or operator of an affected source shall notify the Administrator in writing of the anticipated date for conducting opacity or visible emission observations in accordance with §63.9(f), if such observations are required for the source by a relevant standard.

(5) *Conduct of opacity or visible emission observations.* When a relevant standard under this part includes an opacity or visible emission standard, the owner or operator of an affected source shall comply with the following:

(i) For the purpose of demonstrating initial compliance, opacity or visible emission observations shall be conducted concurrently with the initial performance test required in §63.7 unless one of the following conditions applies:

(A) If no performance test under §63.7 is required, opacity or visible emission observations shall be conducted within 60 days after achieving the maximum production rate at which a new or reconstructed source will be operated, but not later than 120 days after initial startup of the source, or within 120 days after the effective date of the relevant standard in the case of new sources that start up before the standard's effective date. If no performance test under §63.7 is required, opacity or visible emission observations shall be conducted within 120 days after the compliance date for an existing or modified source; or

(B) If visibility or other conditions prevent the opacity or visible emission observations from being conducted concurrently with the initial performance test required under §63.7, or within the time period specified in paragraph (h)(5)(i)(A) of this section, the source's owner or operator shall reschedule the opacity or visible emission observations as soon after the initial performance test, or time period, as possible, but not later than 30 days thereafter, and shall advise the Administrator of the rescheduled date. The rescheduled opacity or visible emission observations shall be conducted (to the extent possible) under the same operating conditions that existed during the initial performance test conducted under §63.7. The visible emissions observer shall determine whether visibility or other conditions prevent the opacity or visible emission observations from being made concurrently with the initial performance test in accordance with procedures contained in Test Method 9 or Test Method 22 in appendix A of part 60 of this chapter.

(ii) For the purpose of demonstrating initial compliance, the minimum total time of opacity observations shall be 3 hours (30 6-minute averages) for the performance test or other required set of observations (e.g., for fugitive-type emission sources subject only to an opacity emission standard).

(iii) The owner or operator of an affected source to which an opacity or visible emission standard in this part applies shall conduct opacity or visible emission observations in accordance with the provisions of this section, record the results of the evaluation of emissions, and report to the Administrator the opacity or visible emission results in accordance with the provisions of §63.10(d).

(iv) [Reserved]

(v) Opacity readings of portions of plumes that contain condensed, uncombined water vapor shall not be used for purposes of determining compliance with opacity emission standards.

(6) *Availability of records.* The owner or operator of an affected source shall make available, upon request by the Administrator, such records that the Administrator deems necessary to determine the conditions under which the visual observations were made and shall provide evidence indicating proof of current visible observer emission certification.

(7) *Use of a continuous opacity monitoring system.* (i) The owner or operator of an affected source required to use a continuous opacity monitoring system (COMS) shall record the monitoring data produced during a performance test required under §63.7 and shall furnish the Administrator a written report of the monitoring results in accordance with the provisions of §63.10(e)(4).

(ii) Whenever an opacity emission test method has not been specified in an applicable subpart, or an owner or operator of an affected source is required to conduct Test Method 9 observations (see appendix A of part 60 of this chapter), the owner or operator may submit, for compliance purposes, COMS data results produced during any performance test required under §63.7 in lieu of Method 9 data. If the owner or operator elects to submit COMS data for compliance with the opacity emission standard, he or she shall notify the Administrator of that decision, in writing, simultaneously with the notification under §63.7(b) of the date the performance test is scheduled to begin. Once the owner or operator of an affected source has notified the Administrator to that effect, the COMS data results will be used to determine opacity compliance during subsequent performance tests required under §63.7, unless the owner or operator notifies the Administrator in writing to the contrary not later than with the notification under §63.7(b) of the date the subsequent performance test is scheduled to begin.

(iii) For the purposes of determining compliance with the opacity emission standard during a performance test required under §63.7 using COMS data, the COMS data shall be reduced to 6-minute averages over the duration of the mass emission performance test.

(iv) The owner or operator of an affected source using a COMS for compliance purposes is responsible for demonstrating that he/she has complied with the performance evaluation requirements of §63.8(e), that the COMS has been properly maintained, operated, and data quality-assured, as specified in §63.8(c) and §63.8(d), and that the resulting data have not been altered in any way.

(v) Except as provided in paragraph (h)(7)(ii) of this section, the results of continuous monitoring by a COMS that indicate that the opacity at the time visual observations were made was not in excess of the emission standard are probative but not conclusive evidence of the actual opacity of an emission, provided that the affected source proves that, at the time of the alleged violation, the instrument used was properly maintained, as specified in §63.8(c), and met Performance Specification 1 in appendix B of part 60 of this chapter, and that the resulting data have not been altered in any way.

(8) *Finding of compliance.* The Administrator will make a finding concerning an affected source's compliance with an opacity or visible emission standard upon obtaining all the compliance information required by the relevant standard (including the written reports of the results of the performance tests required by §63.7, the results of Test Method 9 or another required opacity or visible emission test method, the observer certification required by paragraph (h)(6) of this section, and the continuous opacity monitoring system results, whichever is/are applicable) and any information available to the Administrator needed to determine whether proper operation and maintenance practices are being used.

(9) *Adjustment to an opacity emission standard.* (i) If the Administrator finds under paragraph (h)(8) of this section that an affected source is in compliance with all relevant standards for which initial performance tests were conducted under §63.7, but during the time such performance tests were conducted fails to meet any relevant opacity emission standard, the owner or operator of such source may petition the Administrator to make appropriate adjustment to the opacity emission standard for the affected source. Until the Administrator notifies the owner or operator of the appropriate adjustment, the relevant opacity emission standard remains applicable.

(ii) The Administrator may grant such a petition upon a demonstration by the owner or operator that—

(A) The affected source and its associated air pollution control equipment were operated and maintained in a manner to minimize the opacity of emissions during the performance tests;

(B) The performance tests were performed under the conditions established by the Administrator; and

(C) The affected source and its associated air pollution control equipment were incapable of being adjusted or operated to meet the relevant opacity emission standard.

(iii) The Administrator will establish an adjusted opacity emission standard for the affected source meeting the above requirements at a level at which the source will be able, as indicated by the performance and opacity tests, to meet the opacity emission standard at all times during which the source is meeting the mass or concentration emission standard. The Administrator will promulgate the new opacity emission standard in theFederal Register.

(iv) After the Administrator promulgates an adjusted opacity emission standard for an affected source, the owner or operator of such source shall be subject to the new opacity emission standard, and the new opacity emission standard shall apply to such source during any subsequent performance tests.

(i) *Extension of compliance with emission standards.* (1) Until an extension of compliance has been granted by the Administrator (or a State with an approved permit program) under this paragraph, the owner or operator of an affected source subject to the requirements of this section shall comply with all applicable requirements of this part.

(2) *Extension of compliance for early reductions and other reductions* —(i) *Early reductions.* Pursuant to section 112(i)(5) of the Act, if the owner or operator of an existing source demonstrates that the source has achieved a reduction in emissions of hazardous air pollutants in accordance with the provisions of subpart D of this part, the Administrator (or the State with an approved permit program) will grant the owner or operator an extension of compliance with specific requirements of this part, as specified in subpart D.

(ii) *Other reductions.* Pursuant to section 112(i)(6) of the Act, if the owner or operator of an existing source has installed best available control technology (BACT) (as defined in section 169(3) of the Act) or technology required to meet a lowest achievable emission rate (LAER) (as defined in section 171 of the Act) prior to the promulgation of an emission standard in this part applicable to such source and the same pollutant (or stream of pollutants) controlled pursuant to the BACT or LAER installation, the Administrator will grant the owner or operator an extension of compliance with such emission standard that will apply until the date 5 years after the date on which such installation was achieved, as determined by the Administrator.

(3) *Request for extension of compliance.* Paragraphs (i)(4) through (i)(7) of this section concern requests for an extension of compliance with a relevant standard under this part (except requests for an extension of compliance under paragraph (i)(2)(i) of this section will be handled through procedures specified in subpart D of this part).

(4)(i)(A) The owner or operator of an existing source who is unable to comply with a relevant standard established under this part pursuant to section 112(d) of the Act may request that the Administrator (or a State, when the State has an approved part 70 permit program and the source is required to obtain a part 70 permit under that program, or a State, when the State has been delegated the authority to implement and enforce the emission standard for that source) grant an extension allowing the source up to 1 additional year to comply with the standard, if such additional period is necessary for the installation of controls. An additional extension of up to 3 years may be added for mining waste operations, if the 1-year extension of compliance is insufficient to dry and cover mining waste in order to reduce emissions of any hazardous air pollutant. The owner or operator of an affected source who has requested an extension of compliance under this paragraph and who is otherwise required to obtain a title V permit shall apply for such permit or apply to have the source's title V permit revised to incorporate the conditions of the extension of compliance. The conditions of an extension of compliance granted under this paragraph will be incorporated into the affected source's title V permit according to the provisions of part 70 or Federal title V regulations in this chapter (42 U.S.C. 7661), whichever are applicable.

(B) Any request under this paragraph for an extension of compliance with a relevant standard must be submitted in writing to the appropriate authority no later than 120 days prior to the affected source's compliance date (as specified in paragraphs (b) and (c) of this section), except as provided for in paragraph (i)(4)(i)(C) of this section. Nonfrivolous requests submitted under this paragraph will stay the applicability of the rule as to the emission points in question until such time as the request is granted or denied. A denial will be effective as of the date of denial. Emission standards established under this part may specify alternative dates for the submittal of requests for an extension of compliance if alternatives are appropriate for the source categories affected by those standards.

(C) An owner or operator may submit a compliance extension request after the date specified in paragraph (i)(4)(i)(B) of this section provided the need for the compliance extension arose after that date, and before the otherwise applicable compliance date and the need arose due to circumstances beyond reasonable control of the owner or operator. This request must include, in addition to the information required in paragraph (i)(6)(i) of this section, a statement of the reasons additional time is needed and the date when the owner or operator first learned of the problems. Nonfrivolous requests submitted under this paragraph will stay the applicability of the rule as to the emission points in question until such time as the request is granted or denied. A denial will be effective as of the original compliance date.

(ii) The owner or operator of an existing source unable to comply with a relevant standard established under this part pursuant to section 112(f) of the Act may request that the Administrator grant an extension allowing the source up to 2 years after the standard's effective date to comply with the standard. The Administrator may grant such an extension if he/she finds that such additional period is necessary for the installation of controls and that steps will be taken during the period of the extension to assure that the health of persons will be protected from imminent endangerment. Any request for an extension of compliance with a relevant standard under this paragraph must be submitted in writing to the Administrator not later than 90 calendar days after the effective date of the relevant standard.

(5) The owner or operator of an existing source that has installed BACT or technology required to meet LAER [as specified in paragraph (i)(2)(ii) of this section] prior to the promulgation of a relevant emission standard in this part may request that the Administrator grant an extension allowing the source 5 years from the date on which such installation was achieved, as determined by the Administrator, to comply with the standard. Any request for an extension of compliance with a relevant standard under this paragraph shall be submitted in writing to the Administrator not later than 120 days after the promulgation date of the standard. The Administrator may grant such an extension if he or she finds that the installation of BACT or technology to meet LAER controls the same pollutant (or stream of pollutants) that would be controlled at that source by the relevant emission standard.

(6)(i) The request for a compliance extension under paragraph (i)(4) of this section shall include the following information:

(A) A description of the controls to be installed to comply with the standard;

(B) A compliance schedule, including the date by which each step toward compliance will be reached. At a minimum, the list of dates shall include:

(*1*) The date by which on-site construction, installation of emission control equipment, or a process change is planned to be initiated; and

(*2*) The date by which final compliance is to be achieved.

(*3*) The date by which on-site construction, installation of emission control equipment, or a process change is to be completed; and

(*4*) The date by which final compliance is to be achieved;

(C)—(D)

(ii) The request for a compliance extension under paragraph (i)(5) of this section shall include all information needed to demonstrate to the Administrator's satisfaction that the installation of BACT or technology to meet LAER controls the same pollutant (or stream of pollutants) that would be controlled at that source by the relevant emission standard.

(7) Advice on requesting an extension of compliance may be obtained from the Administrator (or the State with an approved permit program).

(8) *Approval of request for extension of compliance.* Paragraphs (i)(9) through (i)(14) of this section concern approval of an extension of compliance requested under paragraphs (i)(4) through (i)(6) of this section.

(9) Based on the information provided in any request made under paragraphs (i)(4) through (i)(6) of this section, or other information, the Administrator (or the State with an approved permit program) may grant an extension of compliance with an emission standard, as specified in paragraphs (i)(4) and (i)(5) of this section.

(10) The extension will be in writing and will—

(i) Identify each affected source covered by the extension;

(ii) Specify the termination date of the extension;

(iii) Specify the dates by which steps toward compliance are to be taken, if appropriate;

(iv) Specify other applicable requirements to which the compliance extension applies (e.g., performance tests); and

(v)(A) Under paragraph (i)(4), specify any additional conditions that the Administrator (or the State) deems necessary to assure installation of the necessary controls and protection of the health of persons during the extension period; or

(B) Under paragraph (i)(5), specify any additional conditions that the Administrator deems necessary to assure the proper operation and maintenance of the installed controls during the extension period.

(11) The owner or operator of an existing source that has been granted an extension of compliance under paragraph (i)(10) of this section may be required to submit to the Administrator (or the State with an approved permit program) progress reports indicating whether the steps toward compliance outlined in the compliance schedule have been reached. The contents of the progress reports and the dates by which they shall be submitted will be specified in the written extension of compliance granted under paragraph (i)(10) of this section.

(12)(i) The Administrator (or the State with an approved permit program) will notify the owner or operator in writing of approval or intention to deny approval of a request for an extension of compliance within 30 calendar days after receipt of sufficient information to evaluate a request submitted under paragraph (i)(4)(i) or (i)(5) of this section. The Administrator (or the State) will notify the owner or operator in writing of the status of his/her application, that is, whether the application contains sufficient information to make a determination, within 30 calendar days after receipt of the original application and within 30 calendar days after receipt of any supplementary information that is submitted. The 30-day approval or denial period will begin after the owner or operator has been notified in writing that his/her application is complete.

(ii) When notifying the owner or operator that his/her application is not complete, the Administrator will specify the information needed to complete the application and provide notice of opportunity for the applicant to present, in writing, within 30 calendar days after he/she is notified of the incomplete application, additional information or arguments to the Administrator to enable further action on the application.

(iii) Before denying any request for an extension of compliance, the Administrator (or the State with an approved permit program) will notify the owner or operator in writing of the Administrator's (or the State's) intention to issue the denial, together with—

(A) Notice of the information and findings on which the intended denial is based; and

(B) Notice of opportunity for the owner or operator to present in writing, within 15 calendar days after he/she is notified of the intended denial, additional information or arguments to the Administrator (or the State) before further action on the request.

(iv) The Administrator's final determination to deny any request for an extension will be in writing and will set forth the specific grounds on which the denial is based. The final determination will be made within 30 calendar days after presentation of additional information or argument (if the application is complete), or within 30 calendar days after the final date specified for the presentation if no presentation is made.

(13)(i) The Administrator will notify the owner or operator in writing of approval or intention to deny approval of a request for an extension of compliance within 30 calendar days after receipt of sufficient information to evaluate a request submitted under paragraph (i)(4)(ii) of this section. The 30-day approval or denial period will begin after the owner or operator has been notified in writing that his/her application is complete. The Administrator (or the State) will notify the owner or operator in writing of the status of his/her application, that is, whether the application contains sufficient information to make a determination, within 15 calendar days after receipt of the original application and within 15 calendar days after receipt of any supplementary information that is submitted.

(ii) When notifying the owner or operator that his/her application is not complete, the Administrator will specify the information needed to complete the application and provide notice of opportunity for the applicant to present, in writing, within 15 calendar days after he/she is notified of the incomplete application, additional information or arguments to the Administrator to enable further action on the application.

(iii) Before denying any request for an extension of compliance, the Administrator will notify the owner or operator in writing of the Administrator's intention to issue the denial, together with—

(A) Notice of the information and findings on which the intended denial is based; and

(B) Notice of opportunity for the owner or operator to present in writing, within 15 calendar days after he/she is notified of the intended denial, additional information or arguments to the Administrator before further action on the request.

(iv) A final determination to deny any request for an extension will be in writing and will set forth the specific grounds on which the denial is based. The final determination will be made within 30 calendar days after presentation of additional information or argument (if the application is complete), or within 30 calendar days after the final date specified for the presentation if no presentation is made.

(14) The Administrator (or the State with an approved permit program) may terminate an extension of compliance at an earlier date than specified if any specification under paragraph (i)(10)(iii) or (iv) of this section is not met. Upon a determination to terminate, the Administrator will notify, in writing, the owner or operator of the Administrator's determination to terminate, together with:

(i) Notice of the reason for termination; and

(ii) Notice of opportunity for the owner or operator to present in writing, within 15 calendar days after he/she is notified of the determination to terminate, additional information or arguments to the Administrator before further action on the termination.

(iii) A final determination to terminate an extension of compliance will be in writing and will set forth the specific grounds on which the termination is based. The final determination will be made within 30 calendar days after presentation of additional information or arguments, or within 30 calendar days after the final date specified for the presentation if no presentation is made.

(15) [Reserved]

(16) The granting of an extension under this section shall not abrogate the Administrator's authority under section 114 of the Act.

(j) *Exemption from compliance with emission standards.* The President may exempt any stationary source from compliance with any relevant standard established pursuant to section 112 of the Act for a period of not more than 2 years if the President determines that the technology to implement such standard is not available and that it is in the national security interests of the United States to do so. An exemption under this paragraph may be extended for 1 or more additional periods, each period not to exceed 2 years.

[59 FR 12430, Mar. 16, 1994, as amended at 67 FR 16599, Apr. 5, 2002; 68 FR 32600, May 30, 2003; 71 FR 20454, Apr. 20, 2006]

§ 63.7 Performance testing requirements.

(a) *Applicability and performance test dates.* (1) The applicability of this section is set out in §63.1(a)(4).

(2) Except as provided in paragraph (a)(4) of this section, if required to do performance testing by a relevant standard, and unless a waiver of performance testing is obtained under this section or the conditions of paragraph (c)(3)(ii)(B) of this section apply, the owner or operator of the affected source must perform such tests within 180 days of the compliance date for such source.

(i)–(viii) [Reserved]

(ix) Except as provided in paragraph (a)(4) of this section, when an emission standard promulgated under this part is more stringent than the standard proposed (see §63.6(b)(3)), the owner or operator of a new or reconstructed source subject to that standard for which construction or reconstruction is commenced between the proposal and promulgation dates of the standard shall comply with performance testing requirements within 180 days after the standard's effective date, or within 180 days after startup of the source, whichever is later. If the promulgated standard is more stringent than the proposed standard, the owner or operator may choose to demonstrate compliance with either the proposed or the promulgated standard. If the owner or operator chooses to comply with the proposed standard initially, the owner or operator shall conduct a second performance test within 3 years and 180 days after the effective date of the standard, or after startup of the source, whichever is later, to demonstrate compliance with the promulgated standard.

(3) The Administrator may require an owner or operator to conduct performance tests at the affected source at any other time when the action is authorized by section 114 of the Act.

(4) If a force majeure is about to occur, occurs, or has occurred for which the affected owner or operator intends to assert a claim of force majeure:

(i) The owner or operator shall notify the Administrator, in writing as soon as practicable following the date the owner or operator first knew, or through due diligence should have known that the event may cause or caused a delay in testing beyond the regulatory deadline specified in paragraph (a)(2) or (a)(3) of this section, or elsewhere in this part, but the notification must occur before the performance test deadline unless the initial force majeure or a subsequent force majeure event delays the notice, and in such cases, the notification shall occur as soon as practicable.

(ii) The owner or operator shall provide to the Administrator a written description of the force majeure event and a rationale for attributing the delay in testing beyond the regulatory deadline to the force majeure;

describe the measures taken or to be taken to minimize the delay; and identify a date by which the owner or operator proposes to conduct the performance test. The performance test shall be conducted as soon as practicable after the force majeure occurs.

(iii) The decision as to whether or not to grant an extension to the performance test deadline is solely within the discretion of the Administrator. The Administrator will notify the owner or operator in writing of approval or disapproval of the request for an extension as soon as practicable.

(iv) Until an extension of the performance test deadline has been approved by the Administrator under paragraphs (a)(4)(i), (a)(4)(ii), and (a)(4)(iii) of this section, the owner or operator of the affected facility remains strictly subject to the requirements of this part.

(b) *Notification of performance test.* (1) The owner or operator of an affected source must notify the Administrator in writing of his or her intention to conduct a performance test at least 60 calendar days before the performance test is initially scheduled to begin to allow the Administrator, upon request, to review an approve the site-specific test plan required under paragraph (c) of this section and to have an observer present during the test.

(2) In the event the owner or operator is unable to conduct the performance test on the date specified in the notification requirement specified in paragraph (b)(1) of this section due to unforeseeable circumstances beyond his or her control, the owner or operator must notify the Administrator as soon as practicable and without delay prior to the scheduled performance test date and specify the date when the performance test is rescheduled. This notification of delay in conducting the performance test shall not relieve the owner or operator of legal responsibility for compliance with any other applicable provisions of this part or with any other applicable Federal, State, or local requirement, nor will it prevent the Administrator from implementing or enforcing this part or taking any other action under the Act.

(c) *Quality assurance program.* (1) The results of the quality assurance program required in this paragraph will be considered by the Administrator when he/she determines the validity of a performance test.

(2)(i) *Submission of site-specific test plan.* Before conducting a required performance test, the owner or operator of an affected source shall develop and, if requested by the Administrator, shall submit a site-specific test plan to the Administrator for approval. The test plan shall include a test program summary, the test schedule, data quality objectives, and both an internal and external quality assurance (QA) program. Data quality objectives are the pretest expectations of precision, accuracy, and completeness of data.

(ii) The internal QA program shall include, at a minimum, the activities planned by routine operators and analysts to provide an assessment of test data precision; an example of internal QA is the sampling and analysis of replicate samples.

(iii) The external QA program shall include, at a minimum, application of plans for a test method performance audit (PA) during the performance test. The PA's consist of blind audit samples provided by the Administrator and analyzed during the performance test in order to provide a measure of test data bias. The external QA program may also include systems audits that include the opportunity for on-site evaluation by the Administrator of instrument calibration, data validation, sample logging, and documentation of quality control data and field maintenance activities.

(iv) The owner or operator of an affected source shall submit the site-specific test plan to the Administrator upon the Administrator's request at least 60 calendar days before the performance test is scheduled to take place, that is, simultaneously with the notification of intention to conduct a performance test required under paragraph (b) of this section, or on a mutually agreed upon date.

(v) The Administrator may request additional relevant information after the submittal of a site-specific test plan.

(3) *Approval of site-specific test plan.* (i) The Administrator will notify the owner or operator of approval or intention to deny approval of the site-specific test plan (if review of the site-specific test plan is requested) within 30 calendar days after receipt of the original plan and within 30 calendar days after receipt of any

supplementary information that is submitted under paragraph (c)(3)(i)(B) of this section. Before disapproving any site-specific test plan, the Administrator will notify the applicant of the Administrator's intention to disapprove the plan together with—

(A) Notice of the information and findings on which the intended disapproval is based; and

(B) Notice of opportunity for the owner or operator to present, within 30 calendar days after he/she is notified of the intended disapproval, additional information to the Administrator before final action on the plan.

(ii) In the event that the Administrator fails to approve or disapprove the site-specific test plan within the time period specified in paragraph (c)(3)(i) of this section, the following conditions shall apply:

(A) If the owner or operator intends to demonstrate compliance using the test method(s) specified in the relevant standard or with only minor changes to those tests methods (see paragraph (e)(2)(i) of this section), the owner or operator must conduct the performance test within the time specified in this section using the specified method(s);

(B) If the owner or operator intends to demonstrate compliance by using an alternative to any test method specified in the relevant standard, the owner or operator is authorized to conduct the performance test using an alternative test method after the Administrator approves the use of the alternative method when the Administrator approves the site-specific test plan (if review of the site-specific test plan is requested) or after the alternative method is approved (see paragraph (f) of this section). However, the owner or operator is authorized to conduct the performance test using an alternative method in the absence of notification of approval 45 days after submission of the site-specific test plan or request to use an alternative method. The owner or operator is authorized to conduct the performance test within 60 calendar days after he/she is authorized to demonstrate compliance using an alternative test method. Notwithstanding the requirements in the preceding three sentences, the owner or operator may proceed to conduct the performance test as required in this section (without the Administrator's prior approval of the site-specific test plan) if he/she subsequently chooses to use the specified testing and monitoring methods instead of an alternative.

(iii) Neither the submission of a site-specific test plan for approval, nor the Administrator's approval or disapproval of a plan, nor the Administrator's failure to approve or disapprove a plan in a timely manner shall—

(A) Relieve an owner or operator of legal responsibility for compliance with any applicable provisions of this part or with any other applicable Federal, State, or local requirement; or

(B) Prevent the Administrator from implementing or enforcing this part or taking any other action under the Act.

(4)(i) *Performance test method audit program.* The owner or operator must analyze performance audit (PA) samples during each performance test. The owner or operator must request performance audit materials 30 days prior to the test date. Audit materials including cylinder audit gases may be obtained by contacting the appropriate EPA Regional Office or the responsible enforcement authority.

(ii) The Administrator will have sole discretion to require any subsequent remedial actions of the owner or operator based on the PA results.

(iii) If the Administrator fails to provide required PA materials to an owner or operator of an affected source in time to analyze the PA samples during a performance test, the requirement to conduct a PA under this paragraph shall be waived for such source for that performance test. Waiver under this paragraph of the requirement to conduct a PA for a particular performance test does not constitute a waiver of the requirement to conduct a PA for future required performance tests.

(d) *Performance testing facilities.* If required to do performance testing, the owner or operator of each new source and, at the request of the Administrator, the owner or operator of each existing source, shall provide performance testing facilities as follows:

(1) Sampling ports adequate for test methods applicable to such source. This includes:

(i) Constructing the air pollution control system such that volumetric flow rates and pollutant emission rates can be accurately determined by applicable test methods and procedures; and

(ii) Providing a stack or duct free of cyclonic flow during performance tests, as demonstrated by applicable test methods and procedures;

(2) Safe sampling platform(s);

(3) Safe access to sampling platform(s);

(4) Utilities for sampling and testing equipment; and

(5) Any other facilities that the Administrator deems necessary for safe and adequate testing of a source.

(e) *Conduct of performance tests.* (1) Performance tests shall be conducted under such conditions as the Administrator specifies to the owner or operator based on representative performance (i.e., performance based on normal operating conditions) of the affected source. Operations during periods of startup, shutdown, and malfunction shall not constitute representative conditions for the purpose of a performance test, nor shall emissions in excess of the level of the relevant standard during periods of startup, shutdown, and malfunction be considered a violation of the relevant standard unless otherwise specified in the relevant standard or a determination of noncompliance is made under §63.6(e). Upon request, the owner or operator shall make available to the Administrator such records as may be necessary to determine the conditions of performance tests.

(2) Performance tests shall be conducted and data shall be reduced in accordance with the test methods and procedures set forth in this section, in each relevant standard, and, if required, in applicable appendices of parts 51, 60, 61, and 63 of this chapter unless the Administrator—

(i) Specifies or approves, in specific cases, the use of a test method with minor changes in methodology (see definition in §63.90(a)). Such changes may be approved in conjunction with approval of the site-specific test plan (see paragraph (c) of this section); or

(ii) Approves the use of an intermediate or major change or alternative to a test method (see definitions in §63.90(a)), the results of which the Administrator has determined to be adequate for indicating whether a specific affected source is in compliance; or

(iii) Approves shorter sampling times or smaller sample volumes when necessitated by process variables or other factors; or

(iv) Waives the requirement for performance tests because the owner or operator of an affected source has demonstrated by other means to the Administrator's satisfaction that the affected source is in compliance with the relevant standard.

(3) Unless otherwise specified in a relevant standard or test method, each performance test shall consist of three separate runs using the applicable test method. Each run shall be conducted for the time and under the conditions specified in the relevant standard. For the purpose of determining compliance with a relevant standard, the arithmetic mean of the results of the three runs shall apply. Upon receiving approval from the Administrator, results of a test run may be replaced with results of an additional test run in the event that—

(i) A sample is accidentally lost after the testing team leaves the site; or

(ii) Conditions occur in which one of the three runs must be discontinued because of forced shutdown; or

(iii) Extreme meteorological conditions occur; or

(iv) Other circumstances occur that are beyond the owner or operator's control.

(4) Nothing in paragraphs (e)(1) through (e)(3) of this section shall be construed to abrogate the Administrator's authority to require testing under section 114 of the Act.

(f) *Use of an alternative test method* —(1) *General.* Until authorized to use an intermediate or major change or alternative to a test method, the owner or operator of an affected source remains subject to the requirements of this section and the relevant standard.

(2) The owner or operator of an affected source required to do performance testing by a relevant standard may use an alternative test method from that specified in the standard provided that the owner or operator—

(i) Notifies the Administrator of his or her intention to use an alternative test method at least 60 days before the performance test is scheduled to begin;

(ii) Uses Method 301 in appendix A of this part to validate the alternative test method. This may include the use of specific procedures of Method 301 if use of such procedures are sufficient to validate the alternative test method; and

(iii) Submits the results of the Method 301 validation process along with thnotification of intention and the justification for not using the specified test method. The owner or operator may submit the information required in this paragraph well in advance of the deadline specified in paragraph (f)(2)(i) of this section to ensure a timely review by the Administrator in order to meet the performance test date specified in this section or the relevant standard.

(3) The Administrator will determine whether the owner or operator's validation of the proposed alternative test method is adequate and issue an approval or disapproval of the alternative test method. If the owner or operator intends to demonstrate compliance by using an alternative to any test method specified in the relevant standard, the owner or operator is authorized to conduct the performance test using an alternative test method after the Administrator approves the use of the alternative method. However, the owner or operator is authorized to conduct the performance test using an alternative method in the absence of notification of approval/disapproval 45 days after submission of the request to use an alternative method and the request satisfies the requirements in paragraph (f)(2) of this section. The owner or operator is authorized to conduct the performance test within 60 calendar days after he/she is authorized to demonstrate compliance using an alternative test method. Notwithstanding the requirements in the preceding three sentences, the owner or operator may proceed to conduct the performance test as required in this section (without the Administrator's prior approval of the site-specific test plan) if he/she subsequently chooses to use the specified testing and monitoring methods instead of an alternative.

(4) If the Administrator finds reasonable grounds to dispute the results obtained by an alternative test method for the purposes of demonstrating compliance with a relevant standard, the Administrator may require the use of a test method specified in a relevant standard.

(5) If the owner or operator uses an alternative test method for an affected source during a required performance test, the owner or operator of such source shall continue to use the alternative test method for subsequent performance tests at that affected source until he or she receives approval from the Administrator to use another test method as allowed under §63.7(f).

(6) Neither the validation and approval process nor the failure to validate an alternative test method shall abrogate the owner or operator's responsibility to comply with the requirements of this part.

(g) *Data analysis, recordkeeping, and reporting.* (1) Unless otherwise specified in a relevant standard or test method, or as otherwise approved by the Administrator in writing, results of a performance test shall include the analysis of samples, determination of emissions, and raw data. A performance test is "completed" when field sample collection is terminated. The owner or operator of an affected source shall report the results of the performance test to the Administrator before the close of business on the 60th day following the completion of the performance test, unless specified otherwise in a relevant standard or as approved otherwise in writing by the Administrator (see §63.9(i)). The results of the performance test shall be submitted as part of the notification of compliance status required under §63.9(h). Before a title V permit has been issued to the owner or operator of an affected source, the owner or operator shall send the results of the performance test to the Administrator. After a title V permit has been issued to the owner or operator of an affected source, the owner or operator shall send the results of the performance test to the appropriate permitting authority.

(2) [Reserved]

(3) For a minimum of 5 years after a performance test is conducted, the owner or operator shall retain and make available, upon request, for inspection by the Administrator the records or results of such performance test and other data needed to determine emissions from an affected source.

(h) *Waiver of performance tests.* (1) Until a waiver of a performance testing requirement has been granted by the Administrator under this paragraph, the owner or operator of an affected source remains subject to the requirements of this section.

(2) Individual performance tests may be waived upon written application to the Administrator if, in the Administrator's judgment, the source is meeting the relevant standard(s) on a continuous basis, or the source is being operated under an extension of compliance, or the owner or operator has requested an extension of compliance and the Administrator is still considering that request.

(3) *Request to waive a performance test.* (i) If a request is made for an extension of compliance under §63.6(i), the application for a waiver of an initial performance test shall accompany the information required for the request for an extension of compliance. If no extension of compliance is requested or if the owner or operator has requested an extension of compliance and the Administrator is still considering that request, the application for a waiver of an initial performance test shall be submitted at least 60 days before the performance test if the site-specific test plan under paragraph (c) of this section is not submitted.

(ii) If an application for a waiver of a subsequent performance test is made, the application may accompany any required compliance progress report, compliance status report, or excess emissions and continuous monitoring system performance report [such as those required under §63.6(i), §63.9(h), and §63.10(e) or specified in a relevant standard or in the source's title V permit], but it shall be submitted at least 60 days before the performance test if the site-specific test plan required under paragraph (c) of this section is not submitted.

(iii) Any application for a waiver of a performance test shall include information justifying the owner or operator's request for a waiver, such as the technical or economic infeasibility, or the impracticality, of the affected source performing the required test.

(4) *Approval of request to waive performance test.* The Administrator will approve or deny a request for a waiver of a performance test made under paragraph (h)(3) of this section when he/she—

(i) Approves or denies an extension of compliance under §63.6(i)(8); or

(ii) Approves or disapproves a site-specific test plan under §63.7(c)(3); or

(iii) Makes a determination of compliance following the submission of a required compliance status report or excess emissions and continuous monitoring systems performance report; or

(iv) Makes a determination of suitable progress towards compliance following the submission of a compliance progress report, whichever is applicable.

(5) Approval of any waiver granted under this section shall not abrogate the Administrator's authority under the Act or in any way prohibit the Administrator from later canceling the waiver. The cancellation will be made only after notice is given to the owner or operator of the affected source.

[59 FR 12430, Mar. 16, 1994, as amended at 65 FR 62215, Oct. 17, 2000; 67 FR 16602, Apr. 5, 2002; 72 FR 27443, May 16, 2007]

§ 63.8 Monitoring requirements.

(a) *Applicability.* (1) The applicability of this section is set out in §63.1(a)(4).

(2) For the purposes of this part, all CMS required under relevant standards shall be subject to the provisions of this section upon promulgation of performance specifications for CMS as specified in the relevant standard or otherwise by the Administrator.

(3) [Reserved]

(4) Additional monitoring requirements for control devices used to comply with provisions in relevant standards of this part are specified in §63.11.

(b) *Conduct of monitoring.* (1) Monitoring shall be conducted as set forth in this section and the relevant standard(s) unless the Administrator—

(i) Specifies or approves the use of minor changes in methodology for the specified monitoring requirements and procedures (see §63.90(a) for definition); or

(ii) Approves the use of an intermediate or major change or alternative to any monitoring requirements or procedures (see §63.90(a) for definition).

(iii) Owners or operators with flares subject to §63.11(b) are not subject to the requirements of this section unless otherwise specified in the relevant standard.

(2)(i) When the emissions from two or more affected sources are combined before being released to the atmosphere, the owner or operator may install an applicable CMS for each emission stream or for the combined emissions streams, provided the monitoring is sufficient to demonstrate compliance with the relevant standard.

(ii) If the relevant standard is a mass emission standard and the emissions from one affected source are released to the atmosphere through more than one point, the owner or operator must install an applicable CMS at each emission point unless the installation of fewer systems is—

(A) Approved by the Administrator; or

(B) Provided for in a relevant standard (e.g., instead of requiring that a CMS be installed at each emission point before the effluents from those points are channeled to a common control device, the standard specifies that only one CMS is required to be installed at the vent of the control device).

(3) When more than one CMS is used to measure the emissions from one affected source (e.g., multiple breechings, multiple outlets), the owner or operator shall report the results as required for each CMS. However, when one CMS is used as a backup to another CMS, the owner or operator shall report the results from the CMS used to meet the monitoring requirements of this part. If both such CMS are used during a particular reporting period to meet the monitoring requirements of this part, then the owner or operator shall report the results from each CMS for the relevant compliance period.

(c) *Operation and maintenance of continuous monitoring systems.* (1) The owner or operator of an affected source shall maintain and operate each CMS as specified in this section, or in a relevant standard, and in a manner consistent with good air pollution control practices. (i) The owner or operator of an affected source must maintain and operate each CMS as specified in §63.6(e)(1).

(ii) The owner or operator must keep the necessary parts for routine repairs of the affected CMS equipment readily available.

(iii) The owner or operator of an affected source must develop a written startup, shutdown, and malfunction plan for CMS as specified in §63.6(e)(3).

(2)(i) All CMS must be installed such that representative measures of emissions or process parameters from the affected source are obtained. In addition, CEMS must be located according to procedures contained in the applicable performance specification(s).

(ii) Unless the individual subpart states otherwise, the owner or operator must ensure the read out (that portion of the CMS that provides a visual display or record), or other indication of operation, from any CMS required for compliance with the emission standard is readily accessible on site for operational control or inspection by the operator of the equipment.

(3) All CMS shall be installed, operational, and the data verified as specified in the relevant standard either prior to or in conjunction with conducting performance tests under §63.7. Verification of operational status shall, at a minimum, include completion of the manufacturer's written specifications or recommendations for installation, operation, and calibration of the system.

(4) Except for system breakdowns, out-of-control periods, repairs, maintenance periods, calibration checks, and zero (low-level) and high-level calibration drift adjustments, all CMS, including COMS and CEMS, shall be in continuous operation and shall meet minimum frequency of operation requirements as follows:

(i) All COMS shall complete a minimum of one cycle of sampling and analyzing for each successive 10-second period and one cycle of data recording for each successive 6-minute period.

(ii) All CEMS for measuring emissions other than opacity shall complete a minimum of one cycle of operation (sampling, analyzing, and data recording) for each successive 15-minute period.

(5) Unless otherwise approved by the Administrator, minimum procedures for COMS shall include a method for producing a simulated zero opacity condition and an upscale (high-level) opacity condition using a certified neutral density filter or other related technique to produce a known obscuration of the light beam. Such procedures shall provide a system check of all the analyzer's internal optical surfaces and all electronic circuitry, including the lamp and photodetector assembly normally used in the measurement of opacity.

(6) The owner or operator of a CMS that is not a CPMS, which is installed in accordance with the provisions of this part and the applicable CMS performance specification(s), must check the zero (low-level) and high-level calibration drifts at least once daily in accordance with the written procedure specified in the performance evaluation plan developed under paragraphs (e)(3)(i) and (ii) of this section. The zero (low-level) and high-level calibration drifts must be adjusted, at a minimum, whenever the 24-hour zero (low-level) drift exceeds two times the limits of the applicable performance specification(s) specified in the relevant standard. The system shall allow the amount of excess zero (low-level) and high-level drift measured at the 24-hour interval checks to be recorded and quantified whenever specified. For COMS, all optical and instrumental surfaces exposed to the effluent gases must be cleaned prior to performing the zero (low-level) and high-level drift adjustments; the optical surfaces and instrumental surfaces must be cleaned when the cumulative automatic zero compensation, if applicable, exceeds 4 percent opacity. The CPMS must be calibrated prior to use for the purposes of complying with this section. The CPMS must be checked daily for indication that the system is responding. If the CPMS system includes an internal system check, results must be recorded and checked daily for proper operation.

(7)(i) A CMS is out of control if—

(A) The zero (low-level), mid-level (if applicable), or high-level calibration drift (CD) exceeds two times the applicable CD specification in the applicable performance specification or in the relevant standard; or

(B) The CMS fails a performance test audit (e.g., cylinder gas audit), relative accuracy audit, relative accuracy test audit, or linearity test audit; or

(C) The COMS CD exceeds two times the limit in the applicable performance specification in the relevant standard.

(ii) When the CMS is out of control, the owner or operator of the affected source shall take the necessary corrective action and shall repeat all necessary tests which indicate that the system is out of control. The owner or operator shall take corrective action and conduct retesting until the performance requirements are below the applicable limits. The beginning of the out-of-control period is the hour the owner or operator conducts a performance check (e.g., calibration drift) that indicates an exceedance of the performance requirements established under this part. The end of the out-of-control period is the hour following the completion of corrective action and successful demonstration that the system is within the allowable limits. During the period the CMS is out of control, recorded data shall not be used in data averages and calculations, or to meet any data availability requirement established under this part.

(8) The owner or operator of a CMS that is out of control as defined in paragraph (c)(7) of this section shall submit all information concerning out-of-control periods, including start and end dates and hours and descriptions of corrective actions taken, in the excess emissions and continuous monitoring system performance report required in §63.10(e)(3).

(d) *Quality control program.* (1) The results of the quality control program required in this paragraph will be considered by the Administrator when he/she determines the validity of monitoring data.

(2) The owner or operator of an affected source that is required to use a CMS and is subject to the monitoring requirements of this section and a relevant standard shall develop and implement a CMS quality control program. As part of the quality control program, the owner or operator shall develop and submit to the Administrator for approval upon request a site-specific performance evaluation test plan for the CMS performance evaluation required in paragraph (e)(3)(i) of this section, according to the procedures specified in paragraph (e). In addition, each quality control program shall include, at a minimum, a written protocol that describes procedures for each of the following operations:

(i) Initial and any subsequent calibration of the CMS;

(ii) Determination and adjustment of the calibration drift of the CMS;

(iii) Preventive maintenance of the CMS, including spare parts inventory;

(iv) Data recording, calculations, and reporting;

(v) Accuracy audit procedures, including sampling and analysis methods; and

(vi) Program of corrective action for a malfunctioning CMS.

(3) The owner or operator shall keep these written procedures on record for the life of the affected source or until the affected source is no longer subject to the provisions of this part, to be made available for inspection, upon request, by the Administrator. If the performance evaluation plan is revised, the owner or operator shall keep previous (i.e., superseded) versions of the performance evaluation plan on record to be made available for inspection, upon request, by the Administrator, for a period of 5 years after each revision to the plan. Where relevant, e.g., program of corrective action for a malfunctioning CMS, these written procedures may be incorporated as part of the affected source's startup, shutdown, and malfunction plan to avoid duplication of planning and recordkeeping efforts.

(e) *Performance evaluation of continuous monitoring systems* —(1) *General.* When required by a relevant standard, and at any other time the Administrator may require under section 114 of the Act, the owner or operator of an affected source being monitored shall conduct a performance evaluation of the CMS. Such performance evaluation shall be conducted according to the applicable specifications and procedures described in this section or in the relevant standard.

(2) *Notification of performance evaluation.* The owner or operator shall notify the Administrator in writing of the date of the performance evaluation simultaneously with the notification of the performance test date

required under §63.7(b) or at least 60 days prior to the date the performance evaluation is scheduled to begin if no performance test is required.

(3)(i) *Submission of site-specific performance evaluation test plan.* Before conducting a required CMS performance evaluation, the owner or operator of an affected source shall develop and submit a site-specific performance evaluation test plan to the Administrator for approval upon request. The performance evaluation test plan shall include the evaluation program objectives, an evaluation program summary, the performance evaluation schedule, data quality objectives, and both an internal and external QA program. Data quality objectives are the pre-evaluation expectations of precision, accuracy, and completeness of data.

(ii) The internal QA program shall include, at a minimum, the activities planned by routine operators and analysts to provide an assessment of CMS performance. The external QA program shall include, at a minimum, systems audits that include the opportunity for on-site evaluation by the Administrator of instrument calibration, data validation, sample logging, and documentation of quality control data and field maintenance activities.

(iii) The owner or operator of an affected source shall submit the site-specific performance evaluation test plan to the Administrator (if requested) at least 60 days before the performance test or performance evaluation is scheduled to begin, or on a mutually agreed upon date, and review and approval of the performance evaluation test plan by the Administrator will occur with the review and approval of the site-specific test plan (if review of the site-specific test plan is requested).

(iv) The Administrator may request additional relevant information after the submittal of a site-specific performance evaluation test plan.

(v) In the event that the Administrator fails to approve or disapprove the site-specific performance evaluation test plan within the time period specified in §63.7(c)(3), the following conditions shall apply:

(A) If the owner or operator intends to demonstrate compliance using the monitoring method(s) specified in the relevant standard, the owner or operator shall conduct the performance evaluation within the time specified in this subpart using the specified method(s);

(B) If the owner or operator intends to demonstrate compliance by using an alternative to a monitoring method specified in the relevant standard, the owner or operator shall refrain from conducting the performance evaluation until the Administrator approves the use of the alternative method. If the Administrator does not approve the use of the alternative method within 30 days before the performance evaluation is scheduled to begin, the performance evaluation deadlines specified in paragraph (e)(4) of this section may be extended such that the owner or operator shall conduct the performance evaluation within 60 calendar days after the Administrator approves the use of the alternative method. Notwithstanding the requirements in the preceding two sentences, the owner or operator may proceed to conduct the performance evaluation as required in this section (without the Administrator's prior approval of the site-specific performance evaluation test plan) if he/she subsequently chooses to use the specified monitoring method(s) instead of an alternative.

(vi) Neither the submission of a site-specific performance evaluation test plan for approval, nor the Administrator's approval or disapproval of a plan, nor the Administrator's failure to approve or disapprove a plan in a timely manner shall—

(A) Relieve an owner or operator of legal responsibility for compliance with any applicable provisions of this part or with any other applicable Federal, State, or local requirement; or

(B) Prevent the Administrator from implementing or enforcing this part or taking any other action under the Act.

(4) *Conduct of performance evaluation and performance evaluation dates.* The owner or operator of an affected source shall conduct a performance evaluation of a required CMS during any performance test required under §63.7 in accordance with the applicable performance specification as specified in the

relevant standard. Notwithstanding the requirement in the previous sentence, if the owner or operator of an affected source elects to submit COMS data for compliance with a relevant opacity emission standard as provided under §63.6(h)(7), he/she shall conduct a performance evaluation of the COMS as specified in the relevant standard, before the performance test required under §63.7 is conducted in time to submit the results of the performance evaluation as specified in paragraph (e)(5)(ii) of this section. If a performance test is not required, or the requirement for a performance test has been waived under §63.7(h), the owner or operator of an affected source shall conduct the performance evaluation not later than 180 days after the appropriate compliance date for the affected source, as specified in §63.7(a), or as otherwise specified in the relevant standard.

(5) *Reporting performance evaluation results.* (i) The owner or operator shall furnish the Administrator a copy of a written report of the results of the performance evaluation simultaneously with the results of the performance test required under §63.7 or within 60 days of completion of the performance evaluation if no test is required, unless otherwise specified in a relevant standard. The Administrator may request that the owner or operator submit the raw data from a performance evaluation in the report of the performance evaluation results.

(ii) The owner or operator of an affected source using a COMS to determine opacity compliance during any performance test required under §63.7 and described in §63.6(d)(6) shall furnish the Administrator two or, upon request, three copies of a written report of the results of the COMS performance evaluation under this paragraph. The copies shall be provided at least 15 calendar days before the performance test required under §63.7 is conducted.

(f) *Use of an alternative monitoring method.* —(1) *General.* Until permission to use an alternative monitoring procedure (minor, intermediate, or major changes; see definition in §63.90(a)) has been granted by the Administrator under this paragraph (f)(1), the owner or operator of an affected source remains subject to the requirements of this section and the relevant standard.

(2) After receipt and consideration of written application, the Administrator may approve alternatives to any monitoring methods or procedures of this part including, but not limited to, the following:

(i) Alternative monitoring requirements when installation of a CMS specified by a relevant standard would not provide accurate measurements due to liquid water or other interferences caused by substances within the effluent gases;

(ii) Alternative monitoring requirements when the affected source is infrequently operated;

(iii) Alternative monitoring requirements to accommodate CEMS that require additional measurements to correct for stack moisture conditions;

(iv) Alternative locations for installing CMS when the owner or operator can demonstrate that installation at alternate locations will enable accurate and representative measurements;

(v) Alternate methods for converting pollutant concentration measurements to units of the relevant standard;

(vi) Alternate procedures for performing daily checks of zero (low-level) and high-level drift that do not involve use of high-level gases or test cells;

(vii) Alternatives to the American Society for Testing and Materials (ASTM) test methods or sampling procedures specified by any relevant standard;

(viii) Alternative CMS that do not meet the design or performance requirements in this part, but adequately demonstrate a definite and consistent relationship between their measurements and the measurements of opacity by a system complying with the requirements as specified in the relevant standard. The Administrator may require that such demonstration be performed for each affected source; or

(ix) Alternative monitoring requirements when the effluent from a single affected source or the combined effluent from two or more affected sources is released to the atmosphere through more than one point.

(3) If the Administrator finds reasonable grounds to dispute the results obtained by an alternative monitoring method, requirement, or procedure, the Administrator may require the use of a method, requirement, or procedure specified in this section or in the relevant standard. If the results of the specified and alternative method, requirement, or procedure do not agree, the results obtained by the specified method, requirement, or procedure shall prevail.

(4)(i) *Request to use alternative monitoring procedure.* An owner or operator who wishes to use an alternative monitoring procedure must submit an application to the Administrator as described in paragraph (f)(4)(ii) of this section. The application may be submitted at any time provided that the monitoring procedure is not the performance test method used to demonstrate compliance with a relevant standard or other requirement. If the alternative monitoring procedure will serve as the performance test method that is to be used to demonstrate compliance with a relevant standard, the application must be submitted at least 60 days before the performance evaluation is scheduled to begin and must meet the requirements for an alternative test method under §63.7(f).

(ii) The application must contain a description of the proposed alternative monitoring system which addresses the four elements contained in the definition of monitoring in §63.2 and a performance evaluation test plan, if required, as specified in paragraph (e)(3) of this section. In addition, the application must include information justifying the owner or operator's request for an alternative monitoring method, such as the technical or economic infeasibility, or the impracticality, of the affected source using the required method.

(iii) The owner or operator may submit the information required in this paragraph well in advance of the submittal dates specified in paragraph (f)(4)(i) above to ensure a timely review by the Administrator in order to meet the compliance demonstration date specified in this section or the relevant standard.

(iv) Application for minor changes to monitoring procedures, as specified in paragraph (b)(1) of this section, may be made in the site-specific performance evaluation plan.

(5) *Approval of request to use alternative monitoring procedure.* (i) The Administrator will notify the owner or operator of approval or intention to deny approval of the request to use an alternative monitoring method within 30 calendar days after receipt of the original request and within 30 calendar days after receipt of any supplementary information that is submitted. If a request for a minor change is made in conjunction with site-specific performance evaluation plan, then approval of the plan will constitute approval of the minor change. Before disapproving any request to use an alternative monitoring method, the Administrator will notify the applicant of the Administrator's intention to disapprove the request together with—

(A) Notice of the information and findings on which the intended disapproval is based; and

(B) Notice of opportunity for the owner or operator to present additional information to the Administrator before final action on the request. At the time the Administrator notifies the applicant of his or her intention to disapprove the request, the Administrator will specify how much time the owner or operator will have after being notified of the intended disapproval to submit the additional information.

(ii) The Administrator may establish general procedures and criteria in a relevant standard to accomplish the requirements of paragraph (f)(5)(i) of this section.

(iii) If the Administrator approves the use of an alternative monitoring method for an affected source under paragraph (f)(5)(i) of this section, the owner or operator of such source shall continue to use the alternative monitoring method until he or she receives approval from the Administrator to use another monitoring method as allowed by §63.8(f).

(6) *Alternative to the relative accuracy test.* An alternative to the relative accuracy test for CEMS specified in a relevant standard may be requested as follows:

(i) *Criteria for approval of alternative procedures.* An alternative to the test method for determining relative accuracy is available for affected sources with emission rates demonstrated to be less than 50 percent of the relevant standard. The owner or operator of an affected source may petition the Administrator under paragraph (f)(6)(ii) of this section to substitute the relative accuracy test in section 7 of Performance

Specification 2 with the procedures in section 10 if the results of a performance test conducted according to the requirements in §63.7, or other tests performed following the criteria in §63.7, demonstrate that the emission rate of the pollutant of interest in the units of the relevant standard is less than 50 percent of the relevant standard. For affected sources subject to emission limitations expressed as control efficiency levels, the owner or operator may petition the Administrator to substitute the relative accuracy test with the procedures in section 10 of Performance Specification 2 if the control device exhaust emission rate is less than 50 percent of the level needed to meet the control efficiency requirement. The alternative procedures do not apply if the CEMS is used continuously to determine compliance with the relevant standard.

(ii) *Petition to use alternative to relative accuracy test.* The petition to use an alternative to the relative accuracy test shall include a detailed description of the procedures to be applied, the location and the procedure for conducting the alternative, the concentration or response levels of the alternative relative accuracy materials, and the other equipment checks included in the alternative procedure(s). The Administrator will review the petition for completeness and applicability. The Administrator's determination to approve an alternative will depend on the intended use of the CEMS data and may require specifications more stringent than in Performance Specification 2.

(iii) *Rescission of approval to use alternative to relative accuracy test.* The Administrator will review the permission to use an alternative to the CEMS relative accuracy test and may rescind such permission if the CEMS data from a successful completion of the alternative relative accuracy procedure indicate that the affected source's emissions are approaching the level of the relevant standard. The criterion for reviewing the permission is that the collection of CEMS data shows that emissions have exceeded 70 percent of the relevant standard for any averaging period, as specified in the relevant standard. For affected sources subject to emission limitations expressed as control efficiency levels, the criterion for reviewing the permission is that the collection of CEMS data shows that exhaust emissions have exceeded 70 percent of the level needed to meet the control efficiency requirement for any averaging period, as specified in the relevant standard. The owner or operator of the affected source shall maintain records and determine the level of emissions relative to the criterion for permission to use an alternative for relative accuracy testing. If this criterion is exceeded, the owner or operator shall notify the Administrator within 10 days of such occurrence and include a description of the nature and cause of the increased emissions. The Administrator will review the notification and may rescind permission to use an alternative and require the owner or operator to conduct a relative accuracy test of the CEMS as specified in section 7 of Performance Specification 2.

(g) *Reduction of monitoring data.* (1) The owner or operator of each CMS must reduce the monitoring data as specified in paragraphs (g)(1) through (5) of this section.

(2) The owner or operator of each COMS shall reduce all data to 6-minute averages calculated from 36 or more data points equally spaced over each 6-minute period. Data from CEMS for measurement other than opacity, unless otherwise specified in the relevant standard, shall be reduced to 1-hour averages computed from four or more data points equally spaced over each 1-hour period, except during periods when calibration, quality assurance, or maintenance activities pursuant to provisions of this part are being performed. During these periods, a valid hourly average shall consist of at least two data points with each representing a 15-minute period. Alternatively, an arithmetic or integrated 1-hour average of CEMS data may be used. Time periods for averaging are defined in §63.2.

(3) The data may be recorded in reduced or nonreduced form (e.g., ppm pollutant and percent O_2or ng/J of pollutant).

(4) All emission data shall be converted into units of the relevant standard for reporting purposes using the conversion procedures specified in that standard. After conversion into units of the relevant standard, the data may be rounded to the same number of significant digits as used in that standard to specify the emission limit (e.g., rounded to the nearest 1 percent opacity).

(5) Monitoring data recorded during periods of unavoidable CMS breakdowns, out-of-control periods, repairs, maintenance periods, calibration checks, and zero (low-level) and high-level adjustments must not be included in any data average computed under this part. For the owner or operator complying with the requirements of §63.10(b)(2)(vii)(A) or (B), data averages must include any data recorded during periods of monitor breakdown or malfunction.

[59 FR 12430, Mar. 16, 1994, as amended at 64 FR 7468, Feb. 12, 1999; 67 FR 16603, Apr. 5, 2002; 71 FR 20455, Apr. 20, 2006]

§ 63.9 Notification requirements.

(a) *Applicability and general information.* (1) The applicability of this section is set out in §63.1(a)(4).

(2) For affected sources that have been granted an extension of compliance under subpart D of this part, the requirements of this section do not apply to those sources while they are operating under such compliance extensions.

(3) If any State requires a notice that contains all the information required in a notification listed in this section, the owner or operator may send the Administrator a copy of the notice sent to the State to satisfy the requirements of this section for that notification.

(4)(i) Before a State has been delegated the authority to implement and enforce notification requirements established under this part, the owner or operator of an affected source in such State subject to such requirements shall submit notifications to the appropriate Regional Office of the EPA (to the attention of the Director of the Division indicated in the list of the EPA Regional Offices in §63.13).

(ii) After a State has been delegated the authority to implement and enforce notification requirements established under this part, the owner or operator of an affected source in such State subject to such requirements shall submit notifications to the delegated State authority (which may be the same as the permitting authority). In addition, if the delegated (permitting) authority is the State, the owner or operator shall send a copy of each notification submitted to the State to the appropriate Regional Office of the EPA, as specified in paragraph (a)(4)(i) of this section. The Regional Office may waive this requirement for any notifications at its discretion.

(b) *Initial notifications.* (1)(i) The requirements of this paragraph apply to the owner or operator of an affected source when such source becomes subject to a relevant standard.

(ii) If an area source that otherwise would be subject to an emission standard or other requirement established under this part if it were a major source subsequently increases its emissions of hazardous air pollutants (or its potential to emit hazardous air pollutants) such that the source is a major source that is subject to the emission standard or other requirement, such source shall be subject to the notification requirements of this section.

(iii) Affected sources that are required under this paragraph to submit an initial notification may use the application for approval of construction or reconstruction under §63.5(d) of this subpart, if relevant, to fulfill the initial notification requirements of this paragraph.

(2) The owner or operator of an affected source that has an initial startup before the effective date of a relevant standard under this part shall notify the Administrator in writing that the source is subject to the relevant standard. The notification, which shall be submitted not later than 120 calendar days after the effective date of the relevant standard (or within 120 calendar days after the source becomes subject to the relevant standard), shall provide the following information:

(i) The name and address of the owner or operator;

(ii) The address (i.e., physical location) of the affected source;

(iii) An identification of the relevant standard, or other requirement, that is the basis of the notification and the source's compliance date;

(iv) A brief description of the nature, size, design, and method of operation of the source and an identification of the types of emission points within the affected source subject to the relevant standard and types of hazardous air pollutants emitted; and

(v) A statement of whether the affected source is a major source or an area source.

(3) [Reserved]

(4) The owner or operator of a new or reconstructed major affected source for which an application for approval of construction or reconstruction is required under §63.5(d) must provide the following information in writing to the Administrator:

(i) A notification of intention to construct a new major-emitting affected source, reconstruct a major-emitting affected source, or reconstruct a major source such that the source becomes a major-emitting affected source with the application for approval of construction or reconstruction as specified in §63.5(d)(1)(i); and

(ii)–(iv) [Reserved]

(v) A notification of the actual date of startup of the source, delivered or postmarked within 15 calendar days after that date.

(5) The owner or operator of a new or reconstructed affected source for which an application for approval of construction or reconstruction is not required under §63.5(d) must provide the following information in writing to the Administrator:

(i) A notification of intention to construct a new affected source, reconstruct an affected source, or reconstruct a source such that the source becomes an affected source, and

(ii) A notification of the actual date of startup of the source, delivered or postmarked within 15 calendar days after that date.

(iii) Unless the owner or operator has requested and received prior permission from the Administrator to submit less than the information in §63.5(d), the notification must include the information required on the application for approval of construction or reconstruction as specified in §63.5(d)(1)(i).

(c) *Request for extension of compliance.* If the owner or operator of an affected source cannot comply with a relevant standard by the applicable compliance date for that source, or if the owner or operator has installed BACT or technology to meet LAER consistent with §63.6(i)(5) of this subpart, he/she may submit to the Administrator (or the State with an approved permit program) a request for an extension of compliance as specified in §63.6(i)(4) through §63.6(i)(6).

(d) *Notification that source is subject to special compliance requirements.* An owner or operator of a new source that is subject to special compliance requirements as specified in §63.6(b)(3) and §63.6(b)(4) shall notify the Administrator of his/her compliance obligations not later than the notification dates established in paragraph (b) of this section for new sources that are not subject to the special provisions.

(e) *Notification of performance test.* The owner or operator of an affected source shall notify the Administrator in writing of his or her intention to conduct a performance test at least 60 calendar days before the performance test is scheduled to begin to allow the Administrator to review and approve the site-specific test plan required under §63.7(c), if requested by the Administrator, and to have an observer present during the test.

(f) *Notification of opacity and visible emission observations.* The owner or operator of an affected source shall notify the Administrator in writing of the anticipated date for conducting the opacity or visible emission observations specified in §63.6(h)(5), if such observations are required for the source by a relevant standard. The notification shall be submitted with the notification of the performance test date, as specified in paragraph (e) of this section, or if no performance test is required or visibility or other conditions prevent the opacity or visible emission observations from being conducted concurrently with the initial performance test required under §63.7, the owner or operator shall deliver or postmark the notification not less than 30 days before the opacity or visible emission observations are scheduled to take place.

(g) *Additional notification requirements for sources with continuous monitoring systems.* The owner or operator of an affected source required to use a CMS by a relevant standard shall furnish the Administrator written notification as follows:

(1) A notification of the date the CMS performance evaluation under §63.8(e) is scheduled to begin, submitted simultaneously with the notification of the performance test date required under §63.7(b). If no performance test is required, or if the requirement to conduct a performance test has been waived for an affected source under §63.7(h), the owner or operator shall notify the Administrator in writing of the date of the performance evaluation at least 60 calendar days before the evaluation is scheduled to begin;

(2) A notification that COMS data results will be used to determine compliance with the applicable opacity emission standard during a performance test required by §63.7 in lieu of Method 9 or other opacity emissions test method data, as allowed by §63.6(h)(7)(ii), if compliance with an opacity emission standard is required for the source by a relevant standard. The notification shall be submitted at least 60 calendar days before the performance test is scheduled to begin; and

(3) A notification that the criterion necessary to continue use of an alternative to relative accuracy testing, as provided by §63.8(f)(6), has been exceeded. The notification shall be delivered or postmarked not later than 10 days after the occurrence of such exceedance, and it shall include a description of the nature and cause of the increased emissions.

(h) *Notification of compliance status.* (1) The requirements of paragraphs (h)(2) through (h)(4) of this section apply when an affected source becomes subject to a relevant standard.

(2)(i) Before a title V permit has been issued to the owner or operator of an affected source, and each time a notification of compliance status is required under this part, the owner or operator of such source shall submit to the Administrator a notification of compliance status, signed by the responsible official who shall certify its accuracy, attesting to whether the source has complied with the relevant standard. The notification shall list—

(A) The methods that were used to determine compliance;

(B) The results of any performance tests, opacity or visible emission observations, continuous monitoring system (CMS) performance evaluations, and/or other monitoring procedures or methods that were conducted;

(C) The methods that will be used for determining continuing compliance, including a description of monitoring and reporting requirements and test methods;

(D) The type and quantity of hazardous air pollutants emitted by the source (or surrogate pollutants if specified in the relevant standard), reported in units and averaging times and in accordance with the test methods specified in the relevant standard;

(E) If the relevant standard applies to both major and area sources, an analysis demonstrating whether the affected source is a major source (using the emissions data generated for this notification);

(F) A description of the air pollution control equipment (or method) for each emission point, including each control device (or method) for each hazardous air pollutant and the control efficiency (percent) for each control device (or method); and

(G) A statement by the owner or operator of the affected existing, new, or reconstructed source as to whether the source has complied with the relevant standard or other requirements.

(ii) The notification must be sent before the close of business on the 60th day following the completion of the relevant compliance demonstration activity specified in the relevant standard (unless a different reporting period is specified in the standard, in which case the letter must be sent before the close of business on the day the report of the relevant testing or monitoring results is required to be delivered or postmarked). For example, the notification shall be sent before close of business on the 60th (or other required) day following completion of the initial performance test and again before the close of business on the 60th (or other required) day following the completion of any subsequent required performance test. If no performance test is required but opacity or visible emission observations are required to demonstrate compliance with an opacity or visible emission standard under this part, the notification of compliance status shall be sent before close of business on the 30th day following the completion of opacity or visible emission observations. Notifications may be combined as long as the due date requirement for each notification is met.

(3) After a title V permit has been issued to the owner or operator of an affected source, the owner or operator of such source shall comply with all requirements for compliance status reports contained in the source's title V permit, including reports required under this part. After a title V permit has been issued to the owner or operator of an affected source, and each time a notification of compliance status is required under this part, the owner or operator of such source shall submit the notification of compliance status to the appropriate permitting authority following completion of the relevant compliance demonstration activity specified in the relevant standard.

(4) [Reserved]

(5) If an owner or operator of an affected source submits estimates or preliminary information in the application for approval of construction or reconstruction required in §63.5(d) in place of the actual emissions data or control efficiencies required in paragraphs (d)(1)(ii)(H) and (d)(2) of §63.5, the owner or operator shall submit the actual emissions data and other correct information as soon as available but no later than with the initial notification of compliance status required in this section.

(6) Advice on a notification of compliance status may be obtained from the Administrator.

(i) *Adjustment to time periods or postmark deadlines for submittal and review of required communications.* (1)(i) Until an adjustment of a time period or postmark deadline has been approved by the Administrator under paragraphs (i)(2) and (i)(3) of this section, the owner or operator of an affected source remains strictly subject to the requirements of this part.

(ii) An owner or operator shall request the adjustment provided for in paragraphs (i)(2) and (i)(3) of this section each time he or she wishes to change an applicable time period or postmark deadline specified in this part.

(2) Notwithstanding time periods or postmark deadlines specified in this part for the submittal of information to the Administrator by an owner or operator, or the review of such information by the Administrator, such time periods or deadlines may be changed by mutual agreement between the owner or operator and the Administrator. An owner or operator who wishes to request a change in a time period or postmark deadline for a particular requirement shall request the adjustment in writing as soon as practicable before the subject activity is required to take place. The owner or operator shall include in the request whatever information he or she considers useful to convince the Administrator that an adjustment is warranted.

(3) If, in the Administrator's judgment, an owner or operator's request for an adjustment to a particular time period or postmark deadline is warranted, the Administrator will approve the adjustment. The Administrator will notify the owner or operator in writing of approval or disapproval of the request for an adjustment within 15 calendar days of receiving sufficient information to evaluate the request.

(4) If the Administrator is unable to meet a specified deadline, he or she will notify the owner or operator of any significant delay and inform the owner or operator of the amended schedule.

(j) *Change in information already provided.* Any change in the information already provided under this section shall be provided to the Administrator in writing within 15 calendar days after the change.

[59 FR 12430, Mar. 16, 1994, as amended at 64 FR 7468, Feb. 12, 1999; 67 FR 16604, Apr. 5, 2002; 68 FR 32601, May 30, 2003]

§ 63.10 Recordkeeping and reporting requirements.

(a) *Applicability and general information.* (1) The applicability of this section is set out in §63.1(a)(4).

(2) For affected sources that have been granted an extension of compliance under subpart D of this part, the requirements of this section do not apply to those sources while they are operating under such compliance extensions.

(3) If any State requires a report that contains all the information required in a report listed in this section, an owner or operator may send the Administrator a copy of the report sent to the State to satisfy the requirements of this section for that report.

(4)(i) Before a State has been delegated the authority to implement and enforce recordkeeping and reporting requirements established under this part, the owner or operator of an affected source in such State subject to such requirements shall submit reports to the appropriate Regional Office of the EPA (to the attention of the Director of the Division indicated in the list of the EPA Regional Offices in §63.13).

(ii) After a State has been delegated the authority to implement and enforce recordkeeping and reporting requirements established under this part, the owner or operator of an affected source in such State subject to such requirements shall submit reports to the delegated State authority (which may be the same as the permitting authority). In addition, if the delegated (permitting) authority is the State, the owner or operator shall send a copy of each report submitted to the State to the appropriate Regional Office of the EPA, as specified in paragraph (a)(4)(i) of this section. The Regional Office may waive this requirement for any reports at its discretion.

(5) If an owner or operator of an affected source in a State with delegated authority is required to submit periodic reports under this part to the State, and if the State has an established timeline for the submission of periodic reports that is consistent with the reporting frequency(ies) specified for such source under this part, the owner or operator may change the dates by which periodic reports under this part shall be submitted (without changing the frequency of reporting) to be consistent with the State's schedule by mutual agreement between the owner or operator and the State. For each relevant standard established pursuant to section 112 of the Act, the allowance in the previous sentence applies in each State beginning 1 year after the affected source's compliance date for that standard. Procedures governing the implementation of this provision are specified in §63.9(i).

(6) If an owner or operator supervises one or more stationary sources affected by more than one standard established pursuant to section 112 of the Act, he/she may arrange by mutual agreement between the owner or operator and the Administrator (or the State permitting authority) a common schedule on which periodic reports required for each source shall be submitted throughout the year. The allowance in the previous sentence applies in each State beginning 1 year after the latest compliance date for any relevant standard established pursuant to section 112 of the Act for any such affected source(s). Procedures governing the implementation of this provision are specified in §63.9(i).

(7) If an owner or operator supervises one or more stationary sources affected by standards established pursuant to section 112 of the Act (as amended November 15, 1990) and standards set under part 60, part 61, or both such parts of this chapter, he/she may arrange by mutual agreement between the owner or operator and the Administrator (or the State permitting authority) a common schedule on which periodic reports required by each relevant (i.e., applicable) standard shall be submitted throughout the year. The allowance in the previous sentence applies in each State beginning 1 year after the stationary source is required to be in compliance with the relevant section 112 standard, or 1 year after the stationary source is required to be in compliance with the applicable part 60 or part 61 standard, whichever is latest. Procedures governing the implementation of this provision are specified in §63.9(i).

(b) *General recordkeeping requirements.* (1) The owner or operator of an affected source subject to the provisions of this part shall maintain files of all information (including all reports and notifications) required by this part recorded in a form suitable and readily available for expeditious inspection and review. The files shall be retained for at least 5 years following the date of each occurrence, measurement, maintenance, corrective action, report, or record. At a minimum, the most recent 2 years of data shall be retained on site. The remaining 3 years of data may be retained off site. Such files may be maintained on microfilm, on a computer, on computer floppy disks, on magnetic tape disks, or on microfiche.

(2) The owner or operator of an affected source subject to the provisions of this part shall maintain relevant records for such source of—

(i) The occurrence and duration of each startup or shutdown when the startup or shutdown causes the source to exceed any applicable emission limitation in the relevant emission standards;

(ii) The occurrence and duration of each malfunction of operation (*i.e.* , process equipment) or the required air pollution control and monitoring equipment;

(iii) All required maintenance performed on the air pollution control and monitoring equipment;

(iv)(A) Actions taken during periods of startup or shutdown when the source exceeded applicable emission limitations in a relevant standard and when the actions taken are different from the procedures specified in the affected source's startup, shutdown, and malfunction plan (see §63.6(e)(3)); or

(B) Actions taken during periods of malfunction (including corrective actions to restore malfunctioning process and air pollution control and monitoring equipment to its normal or usual manner of operation) when the actions taken are different from the procedures specified in the affected source's startup, shutdown, and malfunction plan (see §63.6(e)(3));

(v) All information necessary, including actions taken, to demonstrate conformance with the affected source's startup, shutdown, and malfunction plan (see §63.6(e)(3)) when all actions taken during periods of startup or shutdown (and the startup or shutdown causes the source to exceed any applicable emission limitation in the relevant emission standards), and malfunction (including corrective actions to restore malfunctioning process and air pollution control and monitoring equipment to its normal or usual manner of operation) are consistent with the procedures specified in such plan. (The information needed to demonstrate conformance with the startup, shutdown, and malfunction plan may be recorded using a "checklist," or some other effective form of recordkeeping, in order to minimize the recordkeeping burden for conforming events);

(vi) Each period during which a CMS is malfunctioning or inoperative (including out-of-control periods);

(vii) All required measurements needed to demonstrate compliance with a relevant standard (including, but not limited to, 15-minute averages of CMS data, raw performance testing measurements, and raw performance evaluation measurements, that support data that the source is required to report);

(A) This paragraph applies to owners or operators required to install a continuous emissions monitoring system (CEMS) where the CEMS installed is automated, and where the calculated data averages do not exclude periods of CEMS breakdown or malfunction. An automated CEMS records and reduces the measured data to the form of the pollutant emission standard through the use of a computerized data acquisition system. In lieu of maintaining a file of all CEMS subhourly measurements as required under paragraph (b)(2)(vii) of this section, the owner or operator shall retain the most recent consecutive three averaging periods of subhourly measurements and a file that contains a hard copy of the data acquisition system algorithm used to reduce the measured data into the reportable form of the standard.

(B) This paragraph applies to owners or operators required to install a CEMS where the measured data is manually reduced to obtain the reportable form of the standard, and where the calculated data averages do not exclude periods of CEMS breakdown or malfunction. In lieu of maintaining a file of all CEMS subhourly measurements as required under paragraph (b)(2)(vii) of this section, the owner or operator shall retain all subhourly measurements for the most recent reporting period. The subhourly measurements shall be retained for 120 days from the date of the most recent summary or excess emission report submitted to the Administrator.

(C) The Administrator or delegated authority, upon notification to the source, may require the owner or operator to maintain all measurements as required by paragraph (b)(2)(vii), if the administrator or the delegated authority determines these records are required to more accurately assess the compliance status of the affected source.

(viii) All results of performance tests, CMS performance evaluations, and opacity and visible emission observations;

(ix) All measurements as may be necessary to determine the conditions of performance tests and performance evaluations;

(x) All CMS calibration checks;

(xi) All adjustments and maintenance performed on CMS;

(xii) Any information demonstrating whether a source is meeting the requirements for a waiver of recordkeeping or reporting requirements under this part, if the source has been granted a waiver under paragraph (f) of this section;

(xiii) All emission levels relative to the criterion for obtaining permission to use an alternative to the relative accuracy test, if the source has been granted such permission under §63.8(f)(6); and

(xiv) All documentation supporting initial notifications and notifications of compliance status under §63.9.

(3) *Recordkeeping requirement for applicability determinations.* If an owner or operator determines that his or her stationary source that emits (or has the potential to emit, without considering controls) one or more hazardous air pollutants regulated by any standard established pursuant to section 112(d) or (f), and that stationary source is in the source category regulated by the relevant standard, but that source is not subject to the relevant standard (or other requirement established under this part) because of limitations on the source's potential to emit or an exclusion, the owner or operator must keep a record of the applicability determination on site at the source for a period of 5 years after the determination, or until the source changes its operations to become an affected source, whichever comes first. The record of the applicability determination must be signed by the person making the determination and include an analysis (or other information) that demonstrates why the owner or operator believes the source is unaffected (e.g., because the source is an area source). The analysis (or other information) must be sufficiently detailed to allow the Administrator to make a finding about the source's applicability status with regard to the relevant standard or other requirement. If relevant, the analysis must be performed in accordance with requirements established in relevant subparts of this part for this purpose for particular categories of stationary sources. If relevant, the analysis should be performed in accordance with EPA guidance materials published to assist sources in making applicability determinations under section 112, if any. The requirements to determine applicability of a standard under §63.1(b)(3) and to record the results of that determination under paragraph (b)(3) of this section shall not by themselves create an obligation for the owner or operator to obtain a title V permit.

(c) *Additional recordkeeping requirements for sources with continuous monitoring systems.* In addition to complying with the requirements specified in paragraphs (b)(1) and (b)(2) of this section, the owner or operator of an affected source required to install a CMS by a relevant standard shall maintain records for such source of—

(1) All required CMS measurements (including monitoring data recorded during unavoidable CMS breakdowns and out-of-control periods);

(2)–(4) [Reserved]

(5) The date and time identifying each period during which the CMS was inoperative except for zero (low-level) and high-level checks;

(6) The date and time identifying each period during which the CMS was out of control, as defined in §63.8(c)(7);

(7) The specific identification (i.e., the date and time of commencement and completion) of each period of excess emissions and parameter monitoring exceedances, as defined in the relevant standard(s), that occurs during startups, shutdowns, and malfunctions of the affected source;

(8) The specific identification (i.e., the date and time of commencement and completion) of each time period of excess emissions and parameter monitoring exceedances, as defined in the relevant standard(s), that occurs during periods other than startups, shutdowns, and malfunctions of the affected source;

(9) [Reserved]

(10) The nature and cause of any malfunction (if known);

(11) The corrective action taken or preventive measures adopted;

(12) The nature of the repairs or adjustments to the CMS that was inoperative or out of control;

(13) The total process operating time during the reporting period; and

(14) All procedures that are part of a quality control program developed and implemented for CMS under §63.8(d).

(15) In order to satisfy the requirements of paragraphs (c)(10) through (c)(12) of this section and to avoid duplicative recordkeeping efforts, the owner or operator may use the affected source's startup, shutdown, and malfunction plan or records kept to satisfy the recordkeeping requirements of the startup, shutdown, and malfunction plan specified in §63.6(e), provided that such plan and records adequately address the requirements of paragraphs (c)(10) through (c)(12).

(d) *General reporting requirements.* (1) Notwithstanding the requirements in this paragraph or paragraph (e) of this section, and except as provided in §63.16, the owner or operator of an affected source subject to reporting requirements under this part shall submit reports to the Administrator in accordance with the reporting requirements in the relevant standard(s).

(2) *Reporting results of performance tests.* Before a title V permit has been issued to the owner or operator of an affected source, the owner or operator shall report the results of any performance test under §63.7 to the Administrator. After a title V permit has been issued to the owner or operator of an affected source, the owner or operator shall report the results of a required performance test to the appropriate permitting authority. The owner or operator of an affected source shall report the results of the performance test to the Administrator (or the State with an approved permit program) before the close of business on the 60th day following the completion of the performance test, unless specified otherwise in a relevant standard or as approved otherwise in writing by the Administrator. The results of the performance test shall be submitted as part of the notification of compliance status required under §63.9(h).

(3) *Reporting results of opacity or visible emission observations.* The owner or operator of an affected source required to conduct opacity or visible emission observations by a relevant standard shall report the opacity or visible emission results (produced using Test Method 9 or Test Method 22, or an alternative to these test methods) along with the results of the performance test required under §63.7. If no performance test is required, or if visibility or other conditions prevent the opacity or visible emission observations from being conducted concurrently with the performance test required under §63.7, the owner or operator shall report the opacity or visible emission results before the close of business on the 30th day following the completion of the opacity or visible emission observations.

(4) *Progress reports.* The owner or operator of an affected source who is required to submit progress reports as a condition of receiving an extension of compliance under §63.6(i) shall submit such reports to the Administrator (or the State with an approved permit program) by the dates specified in the written extension of compliance.

(5)(i) *Periodic startup, shutdown, and malfunction reports.* If actions taken by an owner or operator during a startup or shutdown (and the startup or shutdown causes the source to exceed any applicable emission limitation in the relevant emission standards), or malfunction of an affected source (including actions taken to correct a malfunction) are consistent with the procedures specified in the source's startup, shutdown, and malfunction plan (see §63.6(e)(3)), the owner or operator shall state such information in a startup, shutdown, and malfunction report. Actions taken to minimize emissions during such startups, shutdowns, and malfunctions shall be summarized in the report and may be done in checklist form; if actions taken are the same for each event, only one checklist is necessary. Such a report shall also include the number, duration, and a brief description for each type of malfunction which occurred during the reporting period and which caused or may have caused any applicable emission limitation to be exceeded. Reports shall only be required if a startup or shutdown caused the source to exceed any applicable emission limitation in the relevant emission standards, or if a malfunction occurred during the reporting period. The startup, shutdown, and malfunction report shall consist of a letter, containing the name, title, and signature of the owner or operator or other responsible official who is certifying its accuracy, that shall be submitted to the Administrator semiannually (or on a more frequent basis if specified otherwise in a relevant standard or as established otherwise by the permitting authority in the source's title V permit). The startup, shutdown, and malfunction report shall be delivered or postmarked by the 30th day following the end of each calendar half (or other calendar reporting period, as appropriate). If the owner or operator is required to submit excess emissions and continuous monitoring system performance (or other periodic) reports under this part, the startup, shutdown, and malfunction reports required under this paragraph may be submitted simultaneously with the excess emissions and continuous monitoring system performance (or other) reports. If startup, shutdown, and malfunction reports are submitted with excess emissions and continuous monitoring system performance (or other periodic) reports, and the owner or operator receives approval to reduce the frequency of reporting for the latter under paragraph (e) of this section, the frequency of reporting for the startup, shutdown, and malfunction reports also may be reduced if the Administrator does not object to the intended change. The procedures to implement the allowance in the preceding sentence shall be the same as the procedures specified in paragraph (e)(3) of this section.

(ii) *Immediate startup, shutdown, and malfunction reports.* Notwithstanding the allowance to reduce the frequency of reporting for periodic startup, shutdown, and malfunction reports under paragraph (d)(5)(i) of this section, any time an action taken by an owner or operator during a startup or shutdown that caused the source to exceed any applicable emission limitation in the relevant emission standards, or malfunction (including actions taken to correct a malfunction) is not consistent with the procedures specified in the affected source's startup, shutdown, and malfunction plan, the owner or operator shall report the actions taken for that event within 2 working days after commencing actions inconsistent with the plan followed by a letter within 7 working days after the end of the event. The immediate report required under this paragraph (d)(5)(ii) shall consist of a telephone call (or facsimile (FAX) transmission) to the Administrator within 2 working days after commencing actions inconsistent with the plan, and it shall be followed by a letter, delivered or postmarked within 7 working days after the end of the event, that contains the name, title, and signature of the owner or operator or other responsible official who is certifying its accuracy, explaining the circumstances of the event, the reasons for not following the startup, shutdown, and malfunction plan, describing all excess emissions and/or parameter monitoring exceedances which are believed to have occurred (or could have occurred in the case of malfunctions), and actions taken to minimize emissions in conformance with §63.6(e)(1)(i). Notwithstanding the requirements of the previous sentence, after the effective date of an approved permit program in the State in which an affected source is located, the owner or operator may make alternative reporting arrangements, in advance, with the permitting authority in that State. Procedures governing the arrangement of alternative reporting requirements under this paragraph (d)(5)(ii) are specified in §63.9(i).

(e) *Additional reporting requirements for sources with continuous monitoring systems* —(1) *General.* When more than one CEMS is used to measure the emissions from one affected source (e.g., multiple breechings, multiple outlets), the owner or operator shall report the results as required for each CEMS.

(2) *Reporting results of continuous monitoring system performance evaluations.* (i) The owner or operator of an affected source required to install a CMS by a relevant standard shall furnish the Administrator a copy of a written report of the results of the CMS performance evaluation, as required under §63.8(e), simultaneously with the results of the performance test required under §63.7, unless otherwise specified in the relevant standard.

(ii) The owner or operator of an affected source using a COMS to determine opacity compliance during any performance test required under §63.7 and described in §63.6(d)(6) shall furnish the Administrator two or, upon request, three copies of a written report of the results of the COMS performance evaluation conducted under §63.8(e). The copies shall be furnished at least 15 calendar days before the performance test required under §63.7 is conducted.

(3) *Excess emissions and continuous monitoring system performance report and summary report.* (i) Excess emissions and parameter monitoring exceedances are defined in relevant standards. The owner or operator of an affected source required to install a CMS by a relevant standard shall submit an excess emissions and continuous monitoring system performance report and/or a summary report to the Administrator semiannually, except when—

(A) More frequent reporting is specifically required by a relevant standard;

(B) The Administrator determines on a case-by-case basis that more frequent reporting is necessary to accurately assess the compliance status of the source; or

(C) [Reserved]

(D) The affected source is complying with the Performance Track Provisions of §63.16, which allows less frequent reporting.

(ii) *Request to reduce frequency of excess emissions and continuous monitoring system performance reports.* Notwithstanding the frequency of reporting requirements specified in paragraph (e)(3)(i) of this section, an owner or operator who is required by a relevant standard to submit excess emissions and continuous monitoring system performance (and summary) reports on a quarterly (or more frequent) basis may reduce the frequency of reporting for that standard to semiannual if the following conditions are met:

(A) For 1 full year (e.g., 4 quarterly or 12 monthly reporting periods) the affected source's excess emissions and continuous monitoring system performance reports continually demonstrate that the source is in compliance with the relevant standard;

(B) The owner or operator continues to comply with all recordkeeping and monitoring requirements specified in this subpart and the relevant standard; and

(C) The Administrator does not object to a reduced frequency of reporting for the affected source, as provided in paragraph (e)(3)(iii) of this section.

(iii) The frequency of reporting of excess emissions and continuous monitoring system performance (and summary) reports required to comply with a relevant standard may be reduced only after the owner or operator notifies the Administrator in writing of his or her intention to make such a change and the Administrator does not object to the intended change. In deciding whether to approve a reduced frequency of reporting, the Administrator may review information concerning the source's entire previous performance history during the 5-year recordkeeping period prior to the intended change, including performance test results, monitoring data, and evaluations of an owner or operator's conformance with operation and maintenance requirements. Such information may be used by the Administrator to make a judgment about the source's potential for noncompliance in the future. If the Administrator disapproves the owner or operator's request to reduce the frequency of reporting, the Administrator will notify the owner or operator in writing within 45 days after receiving notice of the owner or operator's intention. The notification from the Administrator to the owner or operator will specify the grounds on which the disapproval is based. In the absence of a notice of disapproval within 45 days, approval is automatically granted.

(iv) As soon as CMS data indicate that the source is not in compliance with any emission limitation or operating parameter specified in the relevant standard, the frequency of reporting shall revert to the frequency specified in the relevant standard, and the owner or operator shall submit an excess emissions and continuous monitoring system performance (and summary) report for the noncomplying emission points at the next appropriate reporting period following the noncomplying event. After demonstrating ongoing compliance with the relevant standard for another full year, the owner or operator may again request approval from the Administrator to reduce the frequency of reporting for that standard, as provided for in paragraphs (e)(3)(ii) and (e)(3)(iii) of this section.

(v) *Content and submittal dates for excess emissions and monitoring system performance reports.* All excess emissions and monitoring system performance reports and all summary reports, if required, shall be delivered or postmarked by the 30th day following the end of each calendar half or quarter, as appropriate.

Written reports of excess emissions or exceedances of process or control system parameters shall include all the information required in paragraphs (c)(5) through (c)(13) of this section, in §63.8(c)(7) and §63.8(c)(8), and in the relevant standard, and they shall contain the name, title, and signature of the responsible official who is certifying the accuracy of the report. When no excess emissions or exceedances of a parameter have occurred, or a CMS has not been inoperative, out of control, repaired, or adjusted, such information shall be stated in the report.

(vi) *Summary report.* As required under paragraphs (e)(3)(vii) and (e)(3)(viii) of this section, one summary report shall be submitted for the hazardous air pollutants monitored at each affected source (unless the relevant standard specifies that more than one summary report is required, e.g., one summary report for each hazardous air pollutant monitored). The summary report shall be entitled "Summary Report—Gaseous and Opacity Excess Emission and Continuous Monitoring System Performance" and shall contain the following information:

(A) The company name and address of the affected source;

(B) An identification of each hazardous air pollutant monitored at the affected source;

(C) The beginning and ending dates of the reporting period;

(D) A brief description of the process units;

(E) The emission and operating parameter limitations specified in the relevant standard(s);

(F) The monitoring equipment manufacturer(s) and model number(s);

(G) The date of the latest CMS certification or audit;

(H) The total operating time of the affected source during the reporting period;

(I) An emission data summary (or similar summary if the owner or operator monitors control system parameters), including the total duration of excess emissions during the reporting period (recorded in minutes for opacity and hours for gases), the total duration of excess emissions expressed as a percent of the total source operating time during that reporting period, and a breakdown of the total duration of excess emissions during the reporting period into those that are due to startup/shutdown, control equipment problems, process problems, other known causes, and other unknown causes;

(J) A CMS performance summary (or similar summary if the owner or operator monitors control system parameters), including the total CMS downtime during the reporting period (recorded in minutes for opacity and hours for gases), the total duration of CMS downtime expressed as a percent of the total source operating time during that reporting period, and a breakdown of the total CMS downtime during the reporting period into periods that are due to monitoring equipment malfunctions, nonmonitoring equipment malfunctions, quality assurance/quality control calibrations, other known causes, and other unknown causes;

(K) A description of any changes in CMS, processes, or controls since the last reporting period;

(L) The name, title, and signature of the responsible official who is certifying the accuracy of the report; and

(M) The date of the report.

(vii) If the total duration of excess emissions or process or control system parameter exceedances for the reporting period is less than 1 percent of the total operating time for the reporting period, and CMS downtime for the reporting period is less than 5 percent of the total operating time for the reporting period, only the summary report shall be submitted, and the full excess emissions and continuous monitoring system performance report need not be submitted unless required by the Administrator.

(viii) If the total duration of excess emissions or process or control system parameter exceedances for the reporting period is 1 percent or greater of the total operating time for the reporting period, or the total CMS downtime for the reporting period is 5 percent or greater of the total operating time for the reporting period, both the summary report and the excess emissions and continuous monitoring system performance report shall be submitted.

(4) *Reporting continuous opacity monitoring system data produced during a performance test.* The owner or operator of an affected source required to use a COMS shall record the monitoring data produced during a performance test required under §63.7 and shall furnish the Administrator a written report of the monitoring results. The report of COMS data shall be submitted simultaneously with the report of the performance test results required in paragraph (d)(2) of this section.

(f) *Waiver of recordkeeping or reporting requirements.* (1) Until a waiver of a recordkeeping or reporting requirement has been granted by the Administrator under this paragraph, the owner or operator of an affected source remains subject to the requirements of this section.

(2) Recordkeeping or reporting requirements may be waived upon written application to the Administrator if, in the Administrator's judgment, the affected source is achieving the relevant standard(s), or the source is operating under an extension of compliance, or the owner or operator has requested an extension of compliance and the Administrator is still considering that request.

(3) If an application for a waiver of recordkeeping or reporting is made, the application shall accompany the request for an extension of compliance under §63.6(i), any required compliance progress report or compliance status report required under this part (such as under §63.6(i) and §63.9(h)) or in the source's title V permit, or an excess emissions and continuous monitoring system performance report required under paragraph (e) of this section, whichever is applicable. The application shall include whatever information the owner or operator considers useful to convince the Administrator that a waiver of recordkeeping or reporting is warranted.

(4) The Administrator will approve or deny a request for a waiver of recordkeeping or reporting requirements under this paragraph when he/she—

(i) Approves or denies an extension of compliance; or

(ii) Makes a determination of compliance following the submission of a required compliance status report or excess emissions and continuous monitoring systems performance report; or

(iii) Makes a determination of suitable progress towards compliance following the submission of a compliance progress report, whichever is applicable.

(5) A waiver of any recordkeeping or reporting requirement granted under this paragraph may be conditioned on other recordkeeping or reporting requirements deemed necessary by the Administrator.

(6) Approval of any waiver granted under this section shall not abrogate the Administrator's authority under the Act or in any way prohibit the Administrator from later canceling the waiver. The cancellation will be made only after notice is given to the owner or operator of the affected source.

[59 FR 12430, Mar. 16, 1994, as amended at 64 FR 7468, Feb. 12, 1999; 67 FR 16604, Apr. 5, 2002; 68 FR 32601, May 30, 2003; 69 FR 21752, Apr. 22, 2004; 71 FR 20455, Apr. 20, 2006]

§ 63.11 Control device requirements.

(a) *Applicability.* The applicability of this section is set out in §63.1(a)(4).

(b) *Flares.* (1) Owners or operators using flares to comply with the provisions of this part shall monitor these control devices to assure that they are operated and maintained in conformance with their designs.

Applicable subparts will provide provisions stating how owners or operators using flares shall monitor these control devices.

(2) Flares shall be steam-assisted, air-assisted, or non-assisted.

(3) Flares shall be operated at all times when emissions may be vented to them.

(4) Flares shall be designed for and operated with no visible emissions, except for periods not to exceed a total of 5 minutes during any 2 consecutive hours. Test Method 22 in appendix A of part 60 of this chapter shall be used to determine the compliance of flares with the visible emission provisions of this part. The observation period is 2 hours and shall be used according to Method 22.

(5) Flares shall be operated with a flame present at all times. The presence of a flare pilot flame shall be monitored using a thermocouple or any other equivalent device to detect the presence of a flame.

(6) An owner/operator has the choice of adhering to the heat content specifications in paragraph (b)(6)(ii) of this section, and the maximum tip velocity specifications in paragraph (b)(7) or (b)(8) of this section, or adhering to the requirements in paragraph (b)(6)(i) of this section.

(i)(A) Flares shall be used that have a diameter of 3 inches or greater, are nonassisted, have a hydrogen content of 8.0 percent (by volume) or greater, and are designed for and operated with an exit velocity less than 37.2 m/sec (122 ft/sec) and less than the velocity V_{max}, as determined by the following equation:

$V_{max}=(X_{H2}-K_1)^* K_2$

Where:

V_{max}=Maximum permitted velocity, m/sec.

K_1=Constant, 6.0 volume-percent hydrogen.

K_2=Constant, 3.9(m/sec)/volume-percent hydrogen.

X_{H2}=The volume-percent of hydrogen, on a wet basis, as calculated by using the American Society for Testing and Materials (ASTM) Method D1946–77. (Incorporated by reference as specified in §63.14).

(B) The actual exit velocity of a flare shall be determined by the method specified in paragraph (b)(7)(i) of this section.

(ii) Flares shall be used only with the net heating value of the gas being combusted at 11.2 MJ/scm (300 Btu/scf) or greater if the flare is steam-assisted or air-assisted; or with the net heating value of the gas being combusted at 7.45 M/scm (200 Btu/scf) or greater if the flares is non-assisted. The net heating value of the gas being combusted in a flare shall be calculated using the following equation:

$$H_T = K\sum_{i=1}^{n} C_i H_i$$

Where:

H_T=Net heating value of the sample, MJ/scm; where the net enthalpy per mole of offgas is based on combustion at 25 °C and 760 mm Hg, but the standard temperature for determining the volume corresponding to one mole is 20 °C.

K=Constant=

$$1.740\times10^{-7}\left(\frac{1}{ppmv}\right)\left(\frac{\text{g-mole}}{\text{scm}}\right)\left(\frac{\text{MJ}}{\text{kcal}}\right)$$

where the standard temperature for (g-mole/scm) is 20 °C.

C_i=Concentration of sample component i in ppmv on a wet basis, as measured for organics by Test Method 18 and measured for hydrogen and carbon monoxide by American Society for Testing and Materials (ASTM) D1946–77 or 90 (Reapproved 1994) (incorporated by reference as specified in §63.14).

H_i=Net heat of combustion of sample component i, kcal/g-mole at 25 °C and 760 mm Hg. The heats of combustion may be determined using ASTM D2382–76 or 88 or D4809–95 (incorporated by reference as specified in §63.14) if published values are not available or cannot be calculated.

n=Number of sample components.

(7)(i) Steam-assisted and nonassisted flares shall be designed for and operated with an exit velocity less than 18.3 m/sec (60 ft/sec), except as provided in paragraphs (b)(7)(ii) and (b)(7)(iii) of this section. The actual exit velocity of a flare shall be determined by dividing by the volumetric flow rate of gas being combusted (in units of emission standard temperature and pressure), as determined by Test Method 2, 2A, 2C, or 2D in appendix A to 40 CFR part 60 of this chapter, as appropriate, by the unobstructed (free) cross-sectional area of the flare tip.

(ii) Steam-assisted and nonassisted flares designed for and operated with an exit velocity, as determined by the method specified in paragraph (b)(7)(i) of this section, equal to or greater than 18.3 m/sec (60 ft/sec) but less than 122 m/sec (400 ft/sec), are allowed if the net heating value of the gas being combusted is greater than 37.3 MJ/scm (1,000 Btu/scf).

(iii) Steam-assisted and nonassisted flares designed for and operated with an exit velocity, as determined by the method specified in paragraph (b)(7)(i) of this section, less than the velocity V_{max}, as determined by the method specified in this paragraph, but less than 122 m/sec (400 ft/sec) are allowed. The maximum permitted velocity, V_{max}, for flares complying with this paragraph shall be determined by the following equation:

$$\mathrm{Log}_{10}(V_{max})=(H_T+28.8)/31.7$$

Where:

V_{max}=Maximum permitted velocity, m/sec.

28.8=Constant.

31.7=Constant.

H_T=The net heating value as determined in paragraph (b)(6) of this section.

(8) Air-assisted flares shall be designed and operated with an exit velocity less than the velocity V_{max}. The maximum permitted velocity, V_{max}, for air-assisted flares shall be determined by the following equation:

$$V_{max}=8.71 + 0.708(H_T)$$

Where:

V_{max}=Maximum permitted velocity, m/sec.

8.71=Constant.

0.708=Constant.

H_T=The net heating value as determined in paragraph (b)(6)(ii) of this section.

[59 FR 12430, Mar. 16, 1994, as amended at 63 FR 24444, May 4, 1998; 65 FR 62215, Oct. 17, 2000; 67 FR 16605, Apr. 5, 2002]

§ 63.12 State authority and delegations.

(a) The provisions of this part shall not be construed in any manner to preclude any State or political subdivision thereof from—

(1) Adopting and enforcing any standard, limitation, prohibition, or other regulation applicable to an affected source subject to the requirements of this part, provided that such standard, limitation, prohibition, or regulation is not less stringent than any requirement applicable to such source established under this part;

(2) Requiring the owner or operator of an affected source to obtain permits, licenses, or approvals prior to initiating construction, reconstruction, modification, or operation of such source; or

(3) Requiring emission reductions in excess of those specified in subpart D of this part as a condition for granting the extension of compliance authorized by section 112(i)(5) of the Act.

(b)(1) Section 112(l) of the Act directs the Administrator to delegate to each State, when appropriate, the authority to implement and enforce standards and other requirements pursuant to section 112 for stationary sources located in that State. Because of the unique nature of radioactive material, delegation of authority to implement and enforce standards that control radionuclides may require separate approval.

(2) Subpart E of this part establishes procedures consistent with section 112(l) for the approval of State rules or programs to implement and enforce applicable Federal rules promulgated under the authority of section 112. Subpart E also establishes procedures for the review and withdrawal of section 112 implementation and enforcement authorities granted through a section 112(l) approval.

(c) All information required to be submitted to the EPA under this part also shall be submitted to the appropriate State agency of any State to which authority has been delegated under section 112(l) of the Act, provided that each specific delegation may exempt sources from a certain Federal or State reporting requirement. The Administrator may permit all or some of the information to be submitted to the appropriate State agency only, instead of to the EPA and the State agency.

§ 63.13 Addresses of State air pollution control agencies and EPA Regional Offices.

(a) All requests, reports, applications, submittals, and other communications to the Administrator pursuant to this part shall be submitted to the appropriate Regional Office of the U.S. Environmental Protection Agency indicated in the following list of EPA Regional Offices.

EPA Region I (Connecticut, Maine, Massachusetts, New Hampshire, Rhode Island, Vermont), Director, Air, Pesticides and Toxics Division, J.F.K. Federal Building, Boston, MA 02203–2211.

EPA Region II (New Jersey, New York, Puerto Rico, Virgin Islands), Director, Air and Waste Management Division, 26 Federal Plaza, New York, NY 10278.

EPA Region III (Delaware, District of Columbia, Maryland, Pennsylvania, Virginia, West Virginia), Director, Air Protection Division, 1650 Arch Street, Philadelphia, PA 19103.

EPA Region IV (Alabama, Florida, Georgia, Kentucky, Mississippi, North Carolina, South Carolina, Tennessee). Director, Air, Pesticides and Toxics Management Division, Atlanta Federal Center, 61 Forsyth Street, Atlanta, GA 30303–3104.

EPA Region V (Illinois, Indiana, Michigan, Minnesota, Ohio, Wisconsin), Director, Air and Radiation Division, 77 West Jackson Blvd., Chicago, IL 60604–3507.

EPA Region VI (Arkansas, Louisiana, New Mexico, Oklahoma, Texas), Director, Air, Pesticides and Toxics, 1445 Ross Avenue, Dallas, TX 75202–2733.

EPA Region VII (Iowa, Kansas, Missouri, Nebraska), Director, Air, RCRA, and Toxics Division, U.S. Environmental Protection Agency, 901 N. 5th Street, Kansas City, KS 66101.

EPA Region VIII (Colorado, Montana, North Dakota, South Dakota, Utah, Wyoming) Director, Air and Toxics Technical Enforcement Program, Office of Enforcement, Compliance and Environmental Justice, Mail Code 8ENF–AT, 1595 Wynkoop Street, Denver, CO 80202–1129.

EPA Region IX (Arizona, California, Hawaii, Nevada, American Samoa, Guam), Director, Air and Toxics Division, 75 Hawthorne Street, San Francisco, CA 94105.

EPA Region X (Alaska, Idaho, Oregon, Washington), Director, Office of Air Quality, 1200 Sixth Avenue (OAQ–107), Seattle, WA 98101.

(b) All information required to be submitted to the Administrator under this part also shall be submitted to the appropriate State agency of any State to which authority has been delegated under section 112(l) of the Act. The owner or operator of an affected source may contact the appropriate EPA Regional Office for the mailing addresses for those States whose delegation requests have been approved.

(c) If any State requires a submittal that contains all the information required in an application, notification, request, report, statement, or other communication required in this part, an owner or operator may send the appropriate Regional Office of the EPA a copy of that submittal to satisfy the requirements of this part for that communication.

[59 FR 12430, Mar. 16, 1994, as amended at 63 FR 66061, Dec. 1, 1998; 67 FR 4184, Jan. 29, 2002; 68 FR 32601, May 30, 2003; 68 FR 35792, June 17, 2003; 73 FR 24871, May 6, 2008]

§ 63.14 Incorporations by reference.

(a) The materials listed in this section are incorporated by reference in the corresponding sections noted. These incorporations by reference were approved by the Director of the Federal Register in accordance with 5 U.S.C. 552(a) and 1 CFR part 51. These materials are incorporated as they exist on the date of the approval, and notice of any change in these materials will be published in theFederal Register.The materials are available for purchase at the corresponding addresses noted below, and all are available for inspection at the National Archives and Records Administration (NARA), at the Air and Radiation Docket and Information Center, U.S. EPA, 401 M St., SW., Washington, DC, and at the EPA Library (MD–35), U.S. EPA, Research Triangle Park, North Carolina. For information on the availability of this material at NARA, call 202–741–6030, or go to: *http://www.archives.gov/federal_register/code_of_federal_regulations/ibr_locations.html.*

(b) The following materials are available for purchase from at least one of the following addresses: American Society for Testing and Materials (ASTM), 100 Barr Harbor Drive, Post Office Box C700, West Conshohocken, PA 19428–2959; or ProQuest, 300 North Zeeb Road, Ann Arbor, MI 48106.

(1) ASTM D523–89, Standard Test Method for Specular Gloss, IBR approved for §63.782.

(2) ASTM D1193–77, 91, Standard Specification for Reagent Water, IBR approved for Appendix A: Method 306, Sections 7.1.1 and 7.4.2.

(3) ASTM D1331–89, Standard Test Methods for Surface and Interfacial Tension of Solutions of Surface Active Agents, IBR approved for Appendix A: Method 306B, Sections 6.2, 11.1, and 12.2.2.

(4) ASTM D1475–90, Standard Test Method for Density of Paint, Varnish Lacquer, and Related Products, IBR approved for §63.788, Appendix A.

(5) ASTM D1946–77, 90, 94, Standard Method for Analysis of Reformed Gas by Gas Chromatography, IBR approved for §63.11(b)(6).

(6) ASTM D2369–93, 95, Standard Test Method for Volatile Content of Coatings, IBR approved for §63.788, Appendix A.

(7) ASTM D2382–76, 88, Heat of Combustion of Hydrocarbon Fuels by Bomb Calorimeter (High-Precision Method), IBR approved for §63.11(b)(6).

(8) ASTM D2879–83, 96, Test Method for Vapor Pressure-Temperature Relationship and Initial Decomposition Temperature of Liquids by Isoteniscope, IBR approved for §63.111 and §63.2406.

(9) ASTM D3257–93, Standard Test Methods for Aromatics in Mineral Spirits by Gas Chromatography, IBR approved for §63.786(b).

(10) ASTM 3695–88, Standard Test Method for Volatile Alcohols in Water by Direct Aqueous-Injection Gas Chromatography, IBR approved for §63.365(e)(1) of Subpart O.

(11) ASTM D3792–91, Standard Method for Water Content of Water-Reducible Paints by Direct Injection into a Gas Chromatograph, IBR approved for §63.788, Appendix A.

(12) ASTM D3912–80, Standard Test Method for Chemical Resistance of Coatings Used in Light-Water Nuclear Power Plants, IBR approved for §63.782.

(13) ASTM D4017–90, 96a, Standard Test Method for Water in Paints and Paint Materials by the Karl Fischer Titration Method, IBR approved for §63.788, Appendix A.

(14) ASTM D4082–89, Standard Test Method for Effects of Gamma Radiation on Coatings for Use in Light-Water Nuclear Power Plants, IBR approved for §63.782.

(15) ASTM D4256–89, 94, Standard Test Method for Determination of the Decontaminability of Coatings Used in Light-Water Nuclear Power Plants, IBR approved for §63.782.

(16) ASTM D4809–95, Standard Test Method for Heat of Combustion of Liquid Hydrocarbon Fuels by Bomb Calorimeter (Precision Method), IBR approved for §63.11(b)(6).

(17) ASTM E180–93, Standard Practice for Determining the Precision of ASTM Methods for Analysis and Testing of Industrial Chemicals, IBR approved for §63.786(b).

(18) ASTM E260–91, 96, General Practice for Packed Column Gas Chromatography, IBR approved for §§63.750(b)(2) and 63.786(b)(5).

(19)–(20) [Reserved]

(21) ASTM D2099–00, Standard Test Method for Dynamic Water Resistance of Shoe Upper Leather by the Maeser Water Penetration Tester, IBR approved for §63.5350.

(22)–(23) [Reserved]

(24) ASTM D2697–86 (Reapproved 1998), “Standard Test Method for Volume Nonvolatile Matter in Clear or Pigmented Coatings,” IBR approved for §§63.3161(f)(1), 63.3521(b)(1), 63.3941(b)(1), 63.4141(b)(1), 63.4741(b)(1), 63.4941(b)(1), and 63.5160(c).

(25) ASTM D6093–97 (Reapproved 2003), “Standard Test Method for Percent Volume Nonvolatile Matter in Clear or Pigmented Coatings Using a Helium Gas Pycnometer,” IBR approved for §§63.3161(f)(1), 63.3521(b)(1), 63.3941(b)(1), 63.4141(b)(1), 63.4741(b)(1), 63.4941(b)(1), and 63.5160(c).

(26) ASTM D1475–98 (Reapproved 2003), “Standard Test Method for Density of Liquid Coatings, Inks, and Related Products,” IBR approved for §§63.3151(b), 63.3941(b)(4), 63.3941(c), 63.3951(c), 63.4141(b)(3), 63.4141(c), and 63.4551(c).

(27) ASTM D6522–00, Standard Test Method for Determination of Nitrogen Oxides, Carbon Monoxide, and Oxygen Concentrations in Emissions from Natural Gas Fired Reciprocating Engines, Combustion Turbines, Boilers, and Process Heaters Using Portable Analyzers,[1] IBR approved for §63.9307(c)(2) and Table 5 to Subpart DDDDD of this part.

(28) ASTM D6420–99 (Reapproved 2004), Standards Test Method for Determination of Gaseous Organic Compounds by Direct Interface Gas Chromatography-Mass Spectometry, IBR approved for §§60.485(g)(5), 60.485a(g)(5), 63.772(a)(1)(ii), 63.2354(b)(3)(i), 63.2354(b)(3)(ii), 63.2354(b)(3)(ii)(A), and 63.2351(b)(3)(ii)(B).

(29) ASTM D6420–99, Standard Test Method for Determination of Gaseous Organic Compounds by Direct Interface Gas Chromatography-Mass Spectrometry, IBR approved for §§63.5799 and 63.5850.

(30) ASTM E 515–95 (Reapproved 2000), Standard Test Method for Leaks Using Bubble Emission Techniques, IBR approved for §63.425(i)(2).

(31) ASTM D5291–02, Standard Test Methods for Instrumental Determination of Carbon, Hydrogen, and Nitrogen in Petroleum Products and Lubricants, IBR approved for §63.3981, appendix A.

(32) ASTM D5965–02, “Standard Test Methods for Specific Gravity of Coating Powders,” IBR approved for §§63.3151(b) and 63.3951(c).

(33) ASTM D6053–00, Standard Test Method for Determination of Volatile Organic Compound (VOC) Content of Electrical Insulating Varnishes, IBR approved for §63.3981, appendix A.

(34) E145–94 (Reapproved 2001), Standard Specification for Gravity-Convection and Forced-Ventilation Ovens, IBR approved for §63.4581, Appendix A.

(35) ASTM D6784–02, Standard Test Method for Elemental, Oxidized, Particle-Bound and Total Mercury in Flue Gas Generated from Coal-Fired Stationary Sources (Ontario Hydro Method),[1] IBR approved for Table 5 to Subpart DDDDD of this part.

(36) ASTM D5066–91 (Reapproved 2001), “Standard Test Method for Determination of the Transfer Efficiency Under Production Conditions for Spray Application of Automotive Paints-Weight Basis,” IBR approved for §63.3161(g).

(37) ASTM D5087–02, “Standard Test Method for Determining Amount of Volatile Organic Compound (VOC) Released from Solventborne Automotive Coatings and Available for Removal in a VOC Control Device (Abatement),” IBR approved for §§63.3165(e) and 63.3176, appendix A.

(38) ASTM D6266–00a, "Test Method for Determining the Amount of Volatile Organic Compound (VOC) Released from Waterborne Automotive Coatings and Available for Removal in a VOC Control Device (Abatement)," IBR approved for §63.3165(e).

(39) ASTM Method D388–99,.[1] Standard Classification of Coals by Rank,[1] IBR approved for §63.7575.

(40) ASTM D396–02a, Standard Specification for Fuel Oils,[1] IBR approved for §63.7575.

(41) ASTM D1835–03a, Standard Specification for Liquified Petroleum (LP) Gases,[1] IBR approved for §63.7575.

(42) ASTM D2013–01, Standard Practice for Preparing Coal Samples for Analysis,[1] IBR approved for Table 6 to Subpart DDDDD of this part.

(43) ASTM D2234–00,.[1] Standard Practice for Collection of a Gross Sample of Coal,[1] IBR approved for Table 6 to Subpart DDDDD of this part.

(44) ASTM D3173–02, Standard Test Method for Moisture in the Analysis Sample of Coal and Coke,[1] IBR approved for Table 6 to Subpart DDDDD of this part.

(45) ASTM D3683–94 (Reapproved 2000), Standard Test Method for Trace Elements in Coal and Coke Ash Absorption,[1] IBR approved for Table 6 to Subpart DDDDD of this part.

(46) ASTM D3684–01, Standard Test Method for Total Mercury in Coal by the Oxygen Bomb Combustion/Atomic Absorption Method,[1] IBR approved for Table 6 to Subpart DDDDD of this part.

(47) ASTM D5198–92 (Reapproved 2003), Standard Practice for Nitric Acid Digestion of Solid Waste,[1] IBR approved for Table 6 to Subpart DDDDD of this part.

(48) ASTM D5865–03a, Standard Test Method for Gross Calorific Value of Coal and Coke,[1] IBR approved for Table 6 to Subpart DDDDD of this part.

(49) ASTM D6323–98 (Reapproved 2003), Standard Guide for Laboratory Subsampling of Media Related to Waste Management Activities,[1] IBR approved for Table 6 to Subpart DDDDD of this part.

(50) ASTM E711–87 (Reapproved 1996), Standard Test Method for Gross Calorific Value of Refuse-Derived Fuel by the Bomb Calorimeter,[1] IBR approved for Table 6 to Subpart DDDDD of this part.

(51) ASTM E776–87 (Reapproved 1996), Standard Test Method for Forms of Chlorine in Refuse-Derived Fuel,[1] IBR approved for Table 6 to Subpart DDDDD of this part.

(52) ASTM E871–82 (Reapproved 1998), Standard Method of Moisture Analysis of Particulate Wood Fuels,[1] IBR approved for Table 6 to Subpart DDDDD of this part.

(53) ASTM E885–88 (Reapproved 1996), Standard Test Methods for Analyses of Metals in Refuse-Derived Fuel by Atomic Absorption Spectroscopy,[1] IBR approved for Table 6 to Subpart DDDDD of this part 63.

(54) ASTM D6348–03, Standard Test Method for Determination of Gaseous Compounds by Extractive Direct Interface Fourier Transform Infrared (FTIR) Spectroscopy, incorporation by reference (IBR) approved for Table 4 to Subpart DDDD of this part as specified in the subpart.

(55) ASTM D2013–04, Standard Practice for Preparing Coal Samples for Analysis, IBR approved for Table 6 to subpart DDDDD of this part.

(56) ASTM D2234–D2234M–03, Standard Practice for Collection of a Gross Sample of Coal, IBR approved for Table 6 to subpart DDDDD of this part.

(57) ASTM D6721–01, Standard Test Method for Determination of Chlorine in Coal by Oxidative Hydrolysis Microcoulometry, IBR approved for Table 6 to subpart DDDDD of this part.

(58) ASTM D3173–03, Standard Test Method for Moisture in the Analysis Sample of Coal and Coke, IBR approved for Table 6 to subpart DDDDD of this part.

(59) ASTM D4606–03, Standard Test Method for Determination of Arsenic and Selenium in Coal by the Hydride Generation/Atomic Absorption Method, IBR approved for Table 6 to subpart DDDDD of this part.

(60) ASTM D6357–04, Standard Test Methods for Determination of Trace Elements in Coal, Coke, and Combustion Residues from Coal Utilization Processes by Inductively Coupled Plasma Atomic Emission Spectrometry, Inductively Coupled Plasma Mass Spectrometry, and Graphite Furnace Atomic Absorption Spectrometry, IBR approved for Table 6 to subpart DDDDD of this part.

(61) ASTM D6722–01, Standard Test Method for Total Mercury in Coal and Coal Combustion Residues by the Direct Combustion Analysis, IBR approved for Table 6 to subpart DDDDD of this part.

(62) ASTM D5865–04, Standard Test Method for Gross Calorific Value of Coal and Coke, IBR approved for Table 6 to subpart DDDDD of this part.

(63) ASTM D2216–05, "Standard Test Methods for Laboratory Determination of Water (Moisture) Content of Soil and Rock by Mass," IBR approved for the definition of "Free organic liquids" in §63.10692.

(64) ASTM D6522–00 (Reapproved 2005), Standard Test Method for Determination of Nitrogen Oxides, Carbon Monoxide, and Oxygen Concentrations in Emissions from Natural Gas Fired Reciprocating Engines, Combustion Turbines, Boilers, and Process Heaters Using Portable Analyzers,[1] IBR approved for Table 4 to Subpart ZZZZ of this part.

(65) ASTM D 5228–92—"Standard Test Method for Determination of Butane Working Capacity of Activated Carbon," reapproved 2005, IBR approved for §63.11092(b)(1)(i)(B)(*1*)(*ii*).

(c) The materials listed below are available for purchase from the American Petroleum Institute (API), 1220 L Street, NW., Washington, DC 20005.

(1) API Publication 2517, Evaporative Loss from External Floating-Roof Tanks, Third Edition, February 1989, IBR approved for §63.111 and §63.2406.

(2) API Publication 2518, Evaporative Loss from Fixed-roof Tanks, Second Edition, October 1991, IBR approved for §63.150(g)(3)(i)(C) of subpart G of this part.

(3) API Manual of Petroleum Measurement Specifications (MPMS) Chapter 19.2, Evaporative Loss From Floating-Roof Tanks (formerly API Publications 2517 and 2519), First Edition, April 1997, IBR approved for §63.1251 of subpart GGG of this part.

(d) *State and Local Requirements*. The materials listed below are available at the Air and Radiation Docket and Information Center, U.S. EPA, 401 M St., SW., Washington, DC. Additionally, the California South Coast Air Quality Management District materials are available at *http://www.aqmd.gov/permit/spraytransferefficiency.html.*

(1) *California Regulatory Requirements Applicable to the Air Toxics Program,* January 5, 1999, IBR approved for §63.99(a)(5)(ii) of subpart E of this part.

(2) New Jersey's *Toxic Catastrophe Prevention Act Program,* (July 20, 1998), Incorporation By Reference approved for §63.99 (a)(30)(i) of subpart E of this part.

(3)(i) Letter of June 7, 1999 to the U.S. Environmental Protection Agency Region 3 from the Delaware Department of Natural Resources and Environmental Control requesting formal full delegation to take over primary responsibility for implementation and enforcement of the Chemical Accident Prevention Program under Section 112(r) of the Clean Air Act Amendments of 1990.

(ii) Delaware Department of Natural Resources and Environmental Control, Division of Air and Waste Management, Accidental Release Prevention Regulation, sections 1 through 5 and sections 7 through 14, effective January 11, 1999, IBR approved for §63.99(a)(8)(i) of subpart E of this part.

(iii) State of Delaware Regulations Governing the Control of Air Pollution (October 2000), IBR approved for §63.99(a)(8)(ii)–(v) of subpart E of this part.

(4) Massachusetts Regulations Applicable to Hazardous Air Pollutants (July 2002). Incorporation By Reference approved for §63.99(a)(21)(ii) of subpart E of this part.

(5)(i) New Hampshire Regulations Applicable to Hazardous Air Pollutants, March, 2003. Incorporation by Reference approved for §63.99(a)(29)(iii) of subpart E of this part.

(ii) New Hampshire Regulations Applicable to Hazardous Air Pollutants, September 2006. Incorporation by Reference approved for §63.99(a)(29)(iv) of subpart E of this part.

(6) Maine Regulations Applicable to Hazardous Air Pollutants (March 2006). Incorporation By Reference approved for §63.99(a)(19)(iii) of subpart E of this part.

(7) California South Coast Air Quality Management District's "Spray Equipment Transfer Efficiency Test Procedure for Equipment User, May 24, 1989", IBR approved for §63.11173(e)(3).

(8) California South Coast Air Quality Management District's "Guidelines for Demonstrating Equivalency with District Approved Transfer Efficient Spray Guns, September 26, 2002", IBR approved for §63.11173(e)

(e) The materials listed below are available for purchase from the National Institute of Standards and Technology, Springfield, VA 22161, (800) 553–6847.

(1) Handbook 44, Specificiations, Tolerances, and Other Technical Requirements for Weighing and Measuring Devices 1998, IBR approved for §63.1303(e)(3).

(2) [Reserved]

(f) The following material is available from the National Council of the Paper Industry for Air and Stream Improvement, Inc. (NCASI), P.O. Box 133318, Research Triangle Park, NC 27709–3318 or at *http://www.ncasi.org.*

(1) NCASI Method DI/MEOH–94.02, Methanol in Process Liquids GC/FID (Gas Chromatography/Flame Ionization Detection), August 1998, Methods Manual, NCASI, Research Triangle Park, NC, IBR approved for §63.457(c)(3)(ii) of subpart S of this part.

(2) NCASI Method CI/WP–98.01, Chilled Impinger Method For Use At Wood Products Mills to Measure Formaldehyde, Methanol, and Phenol, 1998, Methods Manual, NCASI, Research Triangle Park, NC, IBR approved for Table 4 to Subpart DDDD of this part.

(3) NCASI Method IM/CAN/WP–99.02, Impinger/Canister Source Sampling Method for Selected HAPs and Other Compounds at Wood Products Facilities, January 2004, Methods Manual, NCASI, Research Triangle Park, NC, IBR approved for Table 4 to Subpart DDDD of this part.

(4) NCASI Method ISS/FP A105.01, Impinger Source Sampling Method for Selected Aldehydes, Ketones, and Polar Compounds, December 2005, Methods Manual, NCASI, Research Triangle Park, NC, IBR approved for table 4 to subpart DDDD of this part.

(g) The materials listed below are available for purchase from AOAC International, Customer Services, Suite 400, 2200 Wilson Boulevard, Arlington, Virginia, 22201–3301, Telephone (703) 522–3032, Fax (703) 522–5468.

(1) AOAC Official Method 978.01 Phosphorus (Total) in Fertilizers, Automated Method, Sixteenth edition, 1995, IBR approved for §63.626(d)(3)(vi).

(2) AOAC Official Method 969.02 Phosphorus (Total) in Fertilizers, Alkalimetric Quinolinium Molybdophosphate Method, Sixteenth edition, 1995, IBR approved for §63.626(d)(3)(vi).

(3) AOAC Official Method 962.02 Phosphorus (Total) in Fertilizers, Gravimetric Quinolinium Molybdophosphate Method, Sixteenth edition, 1995, IBR approved for §63.626(d)(3)(vi).

(4) AOAC Official Method 957.02 Phosphorus (Total) in Fertilizers, Preparation of Sample Solution, Sixteenth edition, 1995, IBR approved for §63.626(d)(3)(vi).

(5) AOAC Official Method 929.01 Sampling of Solid Fertilizers, Sixteenth edition, 1995, IBR approved for §63.626(d)(3)(vi).

(6) AOAC Official Method 929.02 Preparation of Fertilizer Sample, Sixteenth edition, 1995, IBR approved for §63.626(d)(3)(vi).

(7) AOAC Official Method 958.01 Phosphorus (Total) in Fertilizers, Spectrophotometric Molybdovanadophosphate Method, Sixteenth edition, 1995, IBR approved for §63.626(d)(3)(vi).

(h) The materials listed below are available for purchase from The Association of Florida Phosphate Chemists, P.O. Box 1645, Bartow, Florida, 33830, Book of Methods Used and Adopted By The Association of Florida Phosphate Chemists, Seventh Edition 1991, IBR.

(1) Section IX, Methods of Analysis for Phosphate Rock, No. 1 Preparation of Sample, IBR approved for §63.606(c)(3)(ii) and §63.626(c)(3)(ii).

(2) Section IX, Methods of Analysis for Phosphate Rock, No. 3 Phosphorus—P_2O_5or $Ca_3(PO_4)_2$, Method A-Volumetric Method, IBR approved for §63.606(c)(3)(ii) and §63.626(c)(3)(ii).

(3) Section IX, Methods of Analysis for Phosphate Rock, No. 3 Phosphorus-P_2O_5or $Ca_3(PO_4)_2$, Method B—Gravimetric Quimociac Method, IBR approved for §63.606(c)(3)(ii) and §63.626(c)(3)(ii).

(4) Section IX, Methods of Analysis For Phosphate Rock, No. 3 Phosphorus-P_2O_5or $Ca_3(PO_4)_2$, Method C—Spectrophotometric Method, IBR approved for §63.606(c)(3)(ii) and §63.626(c)(3)(ii).

(5) Section XI, Methods of Analysis for Phosphoric Acid, Superphosphate, Triple Superphosphate, and Ammonium Phosphates, No. 3 Total Phosphorus-P_2O_5, Method A—Volumetric Method, IBR approved for §63.606(c)(3)(ii), §63.626(c)(3)(ii), and §63.626(d)(3)(v).

(6) Section XI, Methods of Analysis for Phosphoric Acid, Superphosphate, Triple Superphosphate, and Ammonium Phosphates, No. 3 Total Phosphorus-P_2O_5, Method B—Gravimetric Quimociac Method, IBR approved for §63.606(c)(3)(ii), §63.626(c)(3)(ii), and §63.626(d)(3)(v).

(7) Section XI, Methods of Analysis for Phosphoric Acid, Superphosphate, Triple Superphosphate, and Ammonium Phosphates, No. 3 Total Phosphorus-P_2O_5, Method C—Spectrophotometric Method, IBR approved for §63.606(c)(3)(ii), §63.626(c)(3)(ii), and §63.626(d)(3)(v).

(i) The following materials are available for purchase from at least one of the following addresses: ASME International, Orders/Inquiries, P.O. Box 2900, Fairfield, NJ 07007–2900; or Global Engineering Documents, Sales Department, 15 Inverness Way East, Englewood, CO 80112.

(1) ANSI/ASME PTC 19.10–1981, "Flue and Exhaust Gas Analyses [Part 10, Instruments and Apparatus]," IBR approved for §§63.309(k)(1)(iii), 63.865(b), 63.3166(a)(3), 63.3360(e)(1)(iii), 63.3545(a)(3), 63.3555(a)(3), 63.4166(a)(3), 63.4362(a)(3), 63.4766(a)(3), 63.4965(a)(3), 63.5160(d)(1)(iii), 63.9307(c)(2), 63.9323(a)(3), 63.11148(e)(3)(iii), 63.11155(e)(3), 63.11162(f)(3)(iii) and (f)(4), 63.11163(g)(1)(iii) and (g)(2), 63.11410(j)(1)(iii), Table 5 to subpart DDDDD of this part, and Table 1 to subpart ZZZZZ of this part.

(2) [Reserved]

(j) The following material is available for purchase from: British Standards Institute, 389 Chiswick High Road, London W4 4AL, United Kingdom.

(1) BS EN 1593:1999, Non-destructive Testing: Leak Testing—Bubble Emission Techniques, IBR approved for §63.425(i)(2).

(2) [Reserved]

(k) The following materials are available for purchase from the National Technical Information Service (NTIS), 5285 Port Royal Road, Springfield, VA 22161, (703) 605–6000 or (800) 553–6847; or for purchase from the Superintendent of Documents, U.S. Government Printing Office, Washington, DC 20402, (202) 512–1800:

(1) The following methods as published in the test methods compendium known as "Test Methods for Evaluating Solid Waste, Physical/Chemical Methods," EPA Publication SW–846, Third Edition. A suffix of "A" in the method number indicates revision one (the method has been revised once). A suffix of "B" in the method number indicates revision two (the method has been revised twice).

(i) Method 0023A, "Sampling Method for Polychlorinated Dibenzo-p-Dioxins and Polychlorinated Dibenzofuran Emissions from Stationary Sources," dated December 1996, IBR approved for §63.1208(b)(1) of Subpart EEE of this part.

(ii) Method 9071B, "n-Hexane Extractable Material (HEM) for Sludge, Sediment, and Solid Samples," dated April 1998, IBR approved for §63.7824(e) of Subpart FFFFF of this part.

(iii) Method 9095A, "Paint Filter Liquids Test," dated December 1996, IBR approved for §§63.7700(b) and 63.7765 of Subpart EEEEE of this part.

(iv) Method 9095B, "Paint Filter Liquids Test," (revision 2), dated November 2004, IBR approved for the definition of "Free organic liquids" in §63.10692, §63.10885(a)(1), and the definition of "Free liquids" in §63.10906.

(2) [Reserved]

(l) The following materials are available for purchase from the American Society of Heating, Refrigerating, and Air-Conditioning Engineers at 1791 Tullie Circle, NE., Atlanta, GA 30329 or by electronic mail at *orders@ashrae.org:*

(1) American Society of Heating, Refrigerating, and Air-Conditioning Engineers Method 52.1, "Gravimetric and Dust-Spot Procedures for Testing Air-Cleaning Devices Used in General Ventilation for Removing Particulate Matter, June 4, 1992", IBR approved for §63.11173(e)(2)(i).

(m) The following materials are available from the California Air Resources Board, Engineering and Certification Branch, 1001 I Street, P.O. Box 2815, Sacramento, CA 95812–2815, Telephone (916) 327–0900 and are also available at the following Web site: *http://www.arb.ca.gov/vapor/vapor.htm.*

(1) California Air Resources Board Vapor Recovery Test Procedure TP–201.1.—"Volumetric Efficiency for Phase I Vapor Recovery Systems," adopted April 12, 1996, and amended February 1, 2001 and October 8, 2003, IBR approved for §63.11120(b)(1).

(2) California Air Resources Board Vapor Recovery Test Procedure TP–201.1E—"Leak Rate and Cracking Pressure of Pressure/Vacuum Vent Valves," adopted October 8, 2003, IBR approved for §63.11120(a)(1)(i).

(3) California Air Resources Board Vapor Recovery Test Procedure TP–201.3—"Determination of 2-Inch WC Static Pressure Performance of Vapor Recovery Systems of Dispensing Facilities," adopted April 12, 1996 and amended March 17, 1999, IBR approved for §63.11120(a)(2)(i).

[59 FR 12430, Mar. 16, 1994]

Editorial Note: ForFederal Registercitations affecting §63.14, see the List of CFR Sections Affected, which appears in the Finding Aids section of the printed volume and on GPO Access.

§ 63.15 Availability of information and confidentiality.

(a) *Availability of information.* (1) With the exception of information protected through part 2 of this chapter, all reports, records, and other information collected by the Administrator under this part are available to the public. In addition, a copy of each permit application, compliance plan (including the schedule of compliance), notification of compliance status, excess emissions and continuous monitoring systems performance report, and title V permit is available to the public, consistent with protections recognized in section 503(e) of the Act.

(2) The availability to the public of information provided to or otherwise obtained by the Administrator under this part shall be governed by part 2 of this chapter.

(b) *Confidentiality.* (1) If an owner or operator is required to submit information entitled to protection from disclosure under section 114(c) of the Act, the owner or operator may submit such information separately. The requirements of section 114(c) shall apply to such information.

(2) The contents of a title V permit shall not be entitled to protection under section 114(c) of the Act; however, information submitted as part of an application for a title V permit may be entitled to protection from disclosure.

§ 63.16 Performance Track Provisions.

(a) Notwithstanding any other requirements in this part, an affected source at any major source or any area source at a Performance Track member facility, which is subject to regular periodic reporting under any subpart of this part, may submit such periodic reports at an interval that is twice the length of the regular period specified in the applicable subparts; provided, that for sources subject to permits under 40 CFR part 70 or 71 no interval so calculated for any report of the results of any required monitoring may be less frequent than once in every six months.

(b) Notwithstanding any other requirements in this part, the modifications of reporting requirements in paragraph (c) of this section apply to any major source at a Performance Track member facility which is subject to requirements under any of the subparts of this part and which has:

(1) Reduced its total HAP emissions to less than 25 tons per year;

(2) Reduced its emissions of each individual HAP to less than 10 tons per year; and

(3) Reduced emissions of all HAPs covered by each MACT standard to at least the level required for full compliance with the applicable emission standard.

(c) For affected sources at any area source at a Performance Track member facility and which meet the requirements of paragraph (b)(3) of this section, or for affected sources at any major source that meet the requirements of paragraph (b) of this section:

(1) If the emission standard to which the affected source is subject is based on add-on control technology, and the affected source complies by using add-on control technology, then all required reporting elements in the periodic report may be met through an annual certification that the affected source is meeting the emission standard by continuing to use that control technology. The affected source must continue to meet all relevant monitoring and recordkeeping requirements. The compliance certification must meet the requirements delineated in Clean Air Act section 114(a)(3).

(2) If the emission standard to which the affected source is subject is based on add-on control technology, and the affected source complies by using pollution prevention, then all required reporting elements in the periodic report may be met through an annual certification that the affected source is continuing to use pollution prevention to reduce HAP emissions to levels at or below those required by the applicable emission standard. The affected source must maintain records of all calculations that demonstrate the level of HAP emissions required by the emission standard as well as the level of HAP emissions achieved by the affected source. The affected source must continue to meet all relevant monitoring and recordkeeping requirements. The compliance certification must meet the requirements delineated in Clean Air Act section 114(a)(3).

(3) If the emission standard to which the affected source is subject is based on pollution prevention, and the affected source complies by using pollution prevention and reduces emissions by an additional 50 percent or greater than required by the applicable emission standard, then all required reporting elements in the periodic report may be met through an annual certification that the affected source is continuing to use pollution prevention to reduce HAP emissions by an additional 50 percent or greater than required by the applicable emission standard. The affected source must maintain records of all calculations that demonstrate the level of HAP emissions required by the emission standard as well as the level of HAP emissions achieved by the affected source. The affected source must continue to meet all relevant monitoring and recordkeeping requirements. The compliance certification must meet the requirements delineated in Clean Air Act section 114(a)(3).

(4) Notwithstanding the provisions of paragraphs (c)(1) through (3), of this section, for sources subject to permits under 40 CFR part 70 or 71, the results of any required monitoring and recordkeeping must be reported not less frequently than once in every six months.

[69 FR 21753, Apr. 22, 2004]

Title 40: Protection of Environment

PART 63—NATIONAL EMISSION STANDARDS FOR HAZARDOUS AIR POLLUTANTS FOR SOURCE CATEGORIES

Subpart B—Requirements for Control Technology Determinations for Major Sources in Accordance With Clean Air Act Sections, Sections 112(g) and 112(j)

Source: 59 FR 26449, May 20, 1994, unless otherwise noted.

§ 63.40 Applicability of §§63.40 through 63.44.

(a) *Applicability.* The requirements of §§63.40 through 63.44 of this subpart carry out section 112(g)(2)(B) of the 1990 Amendments.

(b) *Overall requirements.* The requirements of §§63.40 through 63.44 of this subpart apply to any owner or operator who constructs or reconstructs a major source of hazardous air pollutants after the effective date of section 112(g)(2)(B) (as defined in §63.41) and the effective date of a title V permit program in the State or local jurisdiction in which the major source is (or would be) located unless the major source in question has been specifically regulated or exempted from regulation under a standard issued pursuant to section 112(d), section 112(h), or section 112(j) and incorporated in another subpart of part 63, or the owner or operator of such major source has received all necessary air quality permits for such construction or reconstruction project before the effective date of section 112(g)(2)(B).

(c) *Exclusion for electric utility steam generating units.* The requirements of this subpart do not apply to electric utility steam generating units unless and until such time as these units are added to the source category list pursuant to section 112(c)(5) of the Act.

(d) *Relationship to State and local requirements.* Nothing in this subpart shall prevent a State or local agency from imposing more stringent requirements than those contained in this subpart.

(e) *Exclusion for stationary sources in deleted source categories.* The requirements of this subpart do not apply to stationary sources that are within a source category that has been deleted from the source category list pursuant to section 112(c)(9) of the Act.

(f) *Exclusion for research and development activities.* The requirements of this subpart do not apply to research and development activities, as defined in §63.41.

[61 FR 68399, Dec. 27, 1996]

§ 63.41 Definitions.

Terms used in this subpart that are not defined in this section have the meaning given to them in the Act and in subpart A.

Affected source means the stationary source or group of stationary sources which, when fabricated (on site), erected, or installed meets the definition of "construct a major source" or the definition of "reconstruct a major source" contained in this section.

Affected States are all States:

(1) Whose air quality may be affected and that are contiguous to the State in which a MACT determination is made in accordance with this subpart; or

(2) Whose air quality may be affected and that are within 50 miles of the major source for which a MACT determination is made in accordance with this subpart.

Available information means, for purposes of identifying control technology options for the affected source, information contained in the following information sources as of the date of approval of the MACT determination by the permitting authority:

(1) A relevant proposed regulation, including all supporting information;

(2) Background information documents for a draft or proposed regulation;

(3) Data and information available for the Control Technology Center developed pursuant to section 113 of the Act;

(4) Data and information contained in the Aerometric Informational Retrieval System including information in the MACT data base;

(5) Any additional information that can be expeditiously provided by the Administrator; and

(6) For the purpose of determinations by the permitting authority, any additional information provided by the applicant or others, and any additional information considered available by the permitting authority.

Construct a major source means:

(1) To fabricate, erect, or install at any greenfield site a stationary source or group of stationary sources which is located within a contiguous area and under common control and which emits or has the potential to emit 10 tons per year of any HAP's or 25 tons per year of any combination of HAP, or

(2) To fabricate, erect, or install at any developed site a new process or production unit which in and of itself emits or has the potential to emit 10 tons per year of any HAP or 25 tons per year of any combination of HAP, unless the process or production unit satisfies criteria in paragraphs (2) (i) through (vi) of this definition.

(i) All HAP emitted by the process or production unit that would otherwise be controlled under the requirements of this subpart will be controlled by emission control equipment which was previously installed at the same site as the process or production unit;

(ii) (A) The permitting authority has determined within a period of 5 years prior to the fabrication, erection, or installation of the process or production unit that the existing emission control equipment represented best available control technology (BACT), lowest achievable emission rate (LAER) under 40 CFR part 51 or 52, toxics—best available control technology (T-BACT), or MACT based on State air toxic rules for the category of pollutants which includes those HAP's to be emitted by the process or production unit; or

(B) The permitting authority determines that the control of HAP emissions provided by the existing equipment will be equivalent to that level of control currently achieved by other well-controlled similar sources (i.e., equivalent to the level of control that would be provided by a current BACT, LAER, T-BACT, or State air toxic rule MACT determination);

(iii) The permitting authority determines that the percent control efficiency for emissions of HAP from all sources to be controlled by the existing control equipment will be equivalent to the percent control efficiency provided by the control equipment prior to the inclusion of the new process or production unit;

(iv) The permitting authority has provided notice and an opportunity for public comment concerning its determination that criteria in paragraphs (2)(i), (2)(ii), and (2)(iii) of this definition apply and concerning the continued adequacy of any prior LAER, BATC, T-BACT, or State air toxic rule MACT determination;

(v) If any commenter has asserted that a prior LAER, BACT, T-BACT, or State air toxic rule MACT determination is no longer adequate, the permitting authority has determined that the level of control required by that prior determination remains adequate; and

(vi) Any emission limitations, work practice requirements, or other terms and conditions upon which the above determinations by the permitting authority are applicable requirements under section 504(a) and either have been incorporated into any existing title V permit for the affected facility or will be incorporated into such permit upon issuance.

Control technology means measures, processes, methods, systems, or techniques to limit the emission of hazardous air pollutants through process changes, substitution of materials or other modifications;

(1) Reduce the quantity of, or eliminate emissions of, such pollutants through process changes, substitution of materials or other modifications;

(2) Enclose systems or processes to eliminate emissions;

(3) Collect, capture or treat such pollutants when released from a process, stack, storage or fugitive emissions point;

(4) Are design, equipment, work practice, or operational standards (including requirements for operator training or certification) as provided in 42 U.S.C. 7412(h); or

(5) Are a combination of paragraphs (1) through (4) of this definition.

Effective date of section 112(g)(2)(B) in a State or local jurisdiction means the effective date specified by the permitting authority at the time the permitting authority adopts a program to implement section 112(g) with respect to construction or reconstruction or major sources of HAP, or June 29, 1998 whichever is earlier.

Electric utility steam generating unit means any fossil fuel fired combustion unit of more than 25 megawatts that serves a generator that produces electricity for sale. A unit that co-generates steam and electricity and supplies more than one-third of its potential electric output capacity and more than 25 megawatts electric output to any utility power distribution system for sale shall be considered an electric utility steam generating unit.

Greenfield suite means a contiguous area under common control that is an undeveloped site.

List of Source Categories means the Source Category List required by section 112(c) of the Act.

Maximum achievable control technology (MACT) emission limitation for new sources means the emission limitation which is not less stringent that the emission limitation achieved in practice by the best controlled similar source, and which reflects the maximum degree of deduction in emissions that the permitting authority, taking into consideration the cost of achieving such emission reduction, and any non-air quality health and environmental impacts and energy requirements, determines is achievable by the constructed or reconstructed major source.

Notice of MACT Approval means a document issued by a permitting authority containing all federally enforceable conditions necessary to enforce the application and operation of MACT or other control technologies such that the MACT emission limitation is met.

Permitting authority means the permitting authority as defined in part 70 or 71 of this chapter.

Process or production unit means any collection of structures and/or equipment, that processes assembles, applies, or otherwise uses material inputs to produce or store an intermediate or final product. A single facility may contain more than one process or production unit.

Reconstruct a major source means the replacement of components at an existing process or production unit that in and of itself emits or has that potential to emit 10 tons per year of any HAP or 25 tons per year of any combination of HAP, whenever:

(1) The fixed capital cost of the new components exceeds 50 percent of the fixed capital cost that would be required to construct a comparable process or production unit; and

(2) It is technically and economically feasible for the reconstructed major source to meet the applicable maximum achievable control technology emission limitation for new sources established under this subpart.

Research and development activities means activities conducted at a research or laboratory facility whose primary purpose is to conduct research and development into new processes and products, where such source is operated under the close supervision of technically trained personnel and is not engaged in the manufacture of products for sale or exchange for commercial profit, except in a *de minimis* manner.

Similar source means a stationary source or process that has comparable emissions and is structurally similar in design and capacity to a constructed or reconstructed major source such that the source could be controlled using the same control technology.

[61 FR 68399, Dec. 27, 1996]

§ 63.42 Program requirements governing construction or reconstruction of major sources.

(a) *Adoption of program.* Each permitting authority shall review its existing programs, procedures, and criteria for preconstruction review for conformity to the requirements established by §§63.40 through 63.44, shall make any additions and revisions to its existing programs, procedures, and criteria that the permitting authority deems necessary to properly effectuate §§63.40 through 63.44, and shall adopt a program to implement section 112(g) with respect to construction or reconstruction of major sources of HAP. As part of the adoption by the permitting authority of a program to implement section 112(g) with respect to construction or reconstruction of major sources of HAP, the chief executive officer of the permitting authority shall certify that the program satisfies all applicable requirements established by §§63.40 through 63.44, and shall specify an effective date for that program which is not later than June 29, 1998. Prior to the specified effective date, the permitting authority shall publish a notice stating that the permitting authority has adopted a program to implement section 112(g) with respect to construction or reconstruction of major sources of HAP and stating the effective date, and shall provide a written description of the program to the Administrator through the appropriate EPA Regional Office. Nothing in this section shall be construed either:

(1) To require that any owner or operator of a stationary source comply with any requirement adopted by the permitting authority which is not intended to implement section 112(g) with respect to construction or reconstruction of major sources of HAP; or

(2) To preclude the permitting authority from enforcing any requirements not intended to implement section 112(g) with respect to construction or reconstruction of major sources of HAP under any other provision of applicable law.

(b) *Failure to adopt program.* In the event that the permitting authority fails to adopt a program to implement section 112(g) with respect to construction or reconstruction of major sources of HAP with an effective date on or before June 29, 1998, and the permitting authority concludes that it is able to make case-by-case MACT determinations which conform to the provisions of §63.43 in the absence of such a program, the permitting authority may elect to make such determinations. However, in those instances where the permitting authority elects to make case-by-case MACT determinations in the absence of a program to implement section 112(g) with respect to construction or reconstruction of major sources of HAP, no such case-by-case MACT determination shall take effect until after it has been submitted by the permitting authority in writing to the appropriate EPA Regional Adminstrator and the EPA Regional Administrator has concurred in writing that the case-by-case MACT determination by the permitting authority is in conformity with all requirements established by §§63.40 through 63.44. In the event that the permitting authority fails to adopt a program to implement section 112(g) with respect to construction or reconstruction of major sources of HAP with an effective date on or before June 29, 1998, and the permitting authority concludes that it is unable to make case-by-case MACT determinations in the absence of such a program, the permitting authority may request that the EPA Regional Administrator implement a transitional program to implement section 112(g) with respect to construction or reconstruction of major sources of HAP in the affected State of local jurisdiction while the permitting authority completes development and adoption of a section 112(g) program. Any such transitional section 112(g) program implemented by the EPA Regional Administrator shall conform to all requirements established by §§63.40 through 63.44, and shall remain in effect for no more than 30 months. Continued failure by the permitting authority to adopt a program to implement section 112(g) with respect to construction or reconstruction of major sources of HAP shall be construed as a failure by the permitting authority to adequately administer and enforce its title V permitting program and shall constitute cause by EPA to apply the sanctions and remedies set forth in the Clean Air Act section 502(I).

(c) *Prohibition.* After the effective date of section 112(g)(2)(B) (as defined in §63.41) in a State or local jurisdiction and the effective date of the title V permit program applicable to that State or local jurisdiction, no person may begin actual construction or reconstruction of a major source of HAP in such State or local jurisdiction unless:

(1) The major source in question has been specifically regulated or exempted from regulation under a standard issued pursuant to section 112(d), section 112(h) or section 112(j) in part 63, and the owner and operator has fully complied with all procedures and requirements for preconstruction review established by that standard, including any applicable requirements set forth in subpart A of this part 63; or

(2) The permitting authority has made a final and effective case-by-case determination pursuant to the provisions of §63.43 such that emissions from the constructed or reconstructed major source will be controlled to a level no less stringent than the maximum achievable control technology emission limitation for new sources.

[61 FR 68400, Dec. 27, 1996, as amended at 64 FR 35032, June 30, 1999]

§ 63.43 Maximum achievable control technology (MACT) determinations for constructed and reconstructed major sources.

(a) *Applicability.* The requirements of this section apply to an owner or operator who constructs or reconstructs a major source of HAP subject to a case-by-case determination of maximum achievable control technology pursuant to §63.42(c).

(b) *Requirements for constructed and reconstructed major sources.* When a case-by-case determination of MACT is required by §63.42(c), the owner and operator shall obtain from the permitting authority an approved MACT determination according to one of the review options contained in paragraph (c) of this section.

(c) *Review options.* (1) When the permitting authority requires the owner or operator to obtain, or revise, a permit issued pursuant to title V of the Act before construction or reconstruction of the major source, or when the permitting authority allows the owner or operator at its discretion to obtain or revise such a permit before construction or reconstruction, and the owner or operator elects that option, the owner or operator shall follow the administrative procedures in the program approved under title V of the Act (or in other regulations issued pursuant to title V of the Act, where applicable).

(2) When an owner or operator is not required to obtain or revise a title V permit (or other permit issued pursuant to title V of the Act) before construction or reconstruction, the owner or operator (unless the owner or operator voluntarily follows the process to obtain a title V permit) shall either, at the discretion of the permitting authority:

(i) Apply for and obtain a Notice of MACT Approval according to the procedures outlined in paragraphs (f) through (h) of this section; or

(ii) Apply for a MACT determination under any other administrative procedures for preconstruction review and approval established by the permitting authority for a State or local jurisdiction which provide for public participation in the determination, and ensure that no person may begin actual construction or reconstruction of a major source in that State or local jurisdiction unless the permitting authority determines that the MACT emission limitation for new sources will be met.

(3) When applying for a permit pursuant to title V of the Act, an owner or operator may request approval of case-by-case MACT determinations for alternative operating scenarios. Approval of such determinations satisfies the requirements of section 112(g) of each such scenario.

(4) Regardless of the review process, the MACT emission limitation and requirements established shall be effective as required by paragraph (j) of this section, consistent with the principles established in paragraph (d) of this section, and supported by the information listed in paragraph (e) of this section. The owner or operator shall comply with the requirements in paragraphs (k) and (l) of this section, and with all applicable requirements in subpart A of this part.

(d) *Principles of MACT determinations.* The following general principles shall govern preparation by the owner or operator of each permit application or other application requiring a case-by-case MACT determination concerning construction or reconstruction of a major source, and all subsequent review of and actions taken concerning such an application by the permitting authority:

(1) The MACT emission limitation or MACT requirements recommended by the applicant and approved by the permitting authority shall not be less stringent than the emission control which is achieved in practice by the best controlled similar source, as determined by the permitting authority.

(2) Based upon available information, as defined in this subpart, the MACT emission limitation and control technology (including any requirements under paragraph (d)(3) of this section) recommended by the applicant and approved by the permitting authority shall achieve the maximum degree of reduction in emissions of HAP which can be achieved by utilizing those control technologies that can be identified from the available information, taking into consideration the costs of achieving such emission reduction and any non-air quality health and environmental impacts and energy requirements associated with the emission reduction.

(3) The applicant may recommend a specific design, equipment, work practice, or operational standard, or a combination thereof, and the permitting authority may approve such a standard if the permitting authority specifically determines that it is not feasible to prescribe or enforce an emission limitation under the criteria set forth in section 112(h)(2) of the Act.

(4) If the Administrator has either proposed a relevant emission standard pursuant to section 112(d) or section 112(h) of the Act or adopted a presumptive MACT determination for the source category which includes the constructed or reconstructed major source, then the MACT requirements applied to the constructed or reconstructed major source shall have considered those MACT emission limitations and requirements of the proposed standard or presumptive MACT determination.

(e) *Application requirements for a case-by-case MACT determination.* (1) An application for a MACT determination (whether a permit application under title V of the Act, an application for a Notice of MACT Approval, or other document specified by the permitting authority under paragraph (c)(2)(ii) of this section) shall specify a control technology selected by the owner or operator that, if properly operated and maintained, will meet the MACT emission limitation or standard as determined according to the principles set forth in paragraph (d) of this section.

(2) In each instance where a constructed or reconstructed major source would require additional control technology or a change in control technology, the application for a MACT determination shall contain the following information:

(i) The name and address (physical location) of the major source to be constructed or reconstructed;

(ii) A brief description of the major source to be constructed or reconstructed and identification of any listed source category or categories in which it is included;

(iii) The expected commencement date for the construction or reconstruction of the major source;

(iv) The expected completion date for construction or reconstruction of the major source;

(v) the anticipated date of start-up for the constructed or reconstructed major source;

(vi) The HAP emitted by the constructed or reconstructed major source, and the estimated emission rate for each such HAP, to the extent this information is needed by the permitting authority to determine MACT;

(vii) Any federally enforceable emission limitations applicable to the constructed or reconstructed major source;

(viii) The maximum and expected utilization of capacity of the constructed or reconstructed major source, and the associated uncontrolled emission rates for that source, to the extent this information is needed by the permitting authority to determine MACT;

(ix) The controlled emissions for the constructed or reconstructed major source in tons/yr at expected and maximum utilization of capacity, to the extent this information is needed by the permitting authority to determine MACT;

(x) A recommended emission limitation for the constructed or reconstructed major source consistent with the principles set forth in paragraph (d) of this section;

(xi) The selected control technology to meet the recommended MACT emission limitation, including technical information on the design, operation, size, estimated control efficiency of the control technology (and the manufacturer's name, address, telephone number, and relevant specifications and drawings, if requested by the permitting authority);

(xii) Supporting documentation including identification of alternative control technologies considered by the applicant to meet the emission limitation, and analysis of cost and non-air quality health environmental impacts or energy requirements for the selected control technology; and

(xiii) Any other relevant information required pursuant to subpart A.

(3) In each instance where the owner or operator contends that a constructed or reconstructed major source will be in compliance, upon startup, with case-by-case MACT under this subpart without a change in control technology, the application for a MACT determination shall contain the following information:

(i) The information described in paragraphs (e)(2)(i) through (e)(2)(x) of this section; and

(ii) Documentation of the control technology in place.

(f) *Administrative procedures for review of the Notice of MACT Approval.* (1) The permitting authority will notify the owner or operator in writing, within 45 days from the date the application is first received, as to whether the application for a MACT determination is complete or whether additional information is required.

(2) The permitting authority will initially approve the recommended MACT emission limitation and other terms set forth in the application, or the permitting authority will notify the owner or operator in writing of its intent to disapprove the application, within 30 calendar days after the owner or operator is notified in writing that the application is complete.

(3) The owner or operator may present, in writing, within 60 calendar days after receipt of notice of the permitting authority's intent to disapprove the application, additional information or arguments pertaining to, or amendments to, the application for consideration by the permitting authority before it decides whether to finally disapprove the application.

(4) The permitting authority will either initially approve or issue a final disapproval of the application within 90 days after it notifies the owner or operator of an intent to disapprove or within 30 days after the date additional information is received from the owner or operator; whichever is earlier.

(5) A final determination by the permitting authority to disapprove any application will be in writing and will specify the grounds on which the disapproval is based. If any application is finally disapproved, the owner or operator may submit a subsequent application concerning construction or reconstruction of the same major source, provided that the subsequent application has been amended in response to the stated grounds for the prior disapproval.

(6) An initial decision to approve an application for a MACT determination will be set forth in the Notice of MACT Approval as described in paragraph (g) of this section.

(g) *Notice of MACT Approval.* (1) The Notice of MACT Approval will contain a MACT emission limitation (or a MACT work practice standard if the permitting authority determines it is not feasible to prescribe or enforce an emission standard) to control the emissions of HAP. The MACT emission limitation or standard will be determined by the permitting authority and will conform to the principles set forth in paragraph (d) of this section.

(2) The Notice of MACT Approval will specify any notification, operation and maintenance, performance testing, monitoring, reporting and record keeping requirements. The Notice of MACT Approval shall include:

(i) In addition to the MACT emission limitation or MACT work practice standard established under this subpart, additional emission limits, production limits, operational limits or other terms and conditions necessary to ensure Federal enforceability of the MACT emission limitation;

(ii) Compliance certifications, testing, monitoring, reporting and record keeping requirements that are consistent with the requirements of §70.6(c) of this chapter;

(iii) In accordance with section 114(a)(3) of the Act, monitoring shall be capable of demonstrating continuous compliance during the applicable reporting period. Such monitoring data shall be of sufficient quality to be used as a basis for enforcing all applicable requirements established under this subpart, including emission limitations;

(iv) A statement requiring the owner or operator to comply with all applicable requirements contained in subpart A of this part;

(3) All provisions contained in the Notice of MACT Approval shall be federally enforceable upon the effective date of issuance of such notice, as provided by paragraph (j) of this section.

(4) The Notice of MACT Approval shall expire if construction or reconstruction has not commenced within 18 months of issuance, unless the permitting authority has granted an extension which shall not exceed an additional 12 months.

(h) *Opportunity for public comment on the Notice of MACT Approval.* (1) The permitting authority will provide opportunity for public comment on the Notice of MACT Approval, including, at a minimum:

(i) Availability for public inspection in at least one location in the area affected of the information submitted by the owner or operator and of the permitting authority's initial decision to approve the application;

(ii) A 30-day period for submittal of public comment; and

(iii) A notice by prominent advertisement in the area affected of the location of the source information and initial decision specified in paragraph (h)(1)(i) of this section.

(2) At the discretion of the permitting authority, the Notice of MACT Approval setting forth the initial decision to approve the application may become final automatically at the end of the comment period if no adverse comments are received. If adverse comments are received, the permitting authority shall have 30 days after the end of the comment period to make any necessary revisions in its analysis and decide whether to finally approve the application.

(i) *EPA notification.* The permitting authority shall send a copy of the final Notice of MACT Approval, notice of approval of a title V permit application incorporating a MACT determination (in those instances where the owner or operator either is required or elects to obtain such a permit before construction or reconstruction), or other notice of approval issued pursuant to paragraph (c)(2)(ii) of this section to the Administrator through the appropriate Regional Office, and to all other State and local air pollution control agencies having jurisdiction in affected States.

(j) *Effective date.* The effective date of a MACT determination shall be the date the Notice of MACT Approval becomes final, the date of issuance of a title V permit incorporating a MACT determination (in those instances where the owner or operator either is required or elects to obtain such a permit before construction or reconstruction), or the date any other notice of approval issued pursuant to paragraph (c)(2)(ii) of this section becomes final.

(k) *Compliance date.* On and after the date of start-up, a constructed or reconstructed major source which is subject to the requirements of this subpart shall be in compliance with all applicable requirements specified in the MACT determination.

(l) *Compliance with MACT determinations.* (1) An owner or operator of a constructed or reconstructed major source that is subject to a MACT determination shall comply with all requirements in the final Notice of MACT Approval, the title V permit (in those instances where the owner or operator either is required or elects to obtain such a permit before construction or reconstruction), or any other final notice of approval issued pursuant to paragraph (c)(2)(ii) of this section, including but not limited to any MACT emission limitation or MACT work practice standard, and any notification, operation and maintenance, performance testing, monitoring, reporting, and recordkeeping requirements.

(2) An owner or operator of a constructed or reconstructed major source which has obtained a MACT determination shall be deemed to be in compliance with section 112(g)(2)(B) of the Act only to the extent that the constructed or reconstructed major source is in compliance with all requirements set forth in the final Notice of MACT Approval, the title V permit (in those instances where the owner or operator either is required or elects to obtain such a permit before construction or reconstruction), or any other final notice of approval issued pursuant to paragraph (c)(2)(ii) of this section. Any violation of such requirements by the owner or operator shall be deemed by the permitting authority and by EPA to be a violation of the prohibition on construction or reconstruction in section 112(g)(2)(B) for whatever period the owner or operator is determined to be in violation of such requirements, and shall subject the owner or operator to appropriate enforcement action under the Act.

(m) *Reporting to the Administrator.* Within 60 days of the issuance of a final Notice of MACT Approval, a title V permit incorporating a MACT determination (in those instances where the owner or operator either is required or elects to obtain such a permit before construction or reconstruction), or any other final notice of approval issued pursuant to paragraph (c)(2)(ii) of this section, the permitting authority shall provide a copy of such notice to the Administrator, and shall provide a summary in a compatible electronic format for inclusion in the MACT data base.

[20 FR 68401, Dec. 27, 1996]

§ 63.44 Requirements for constructed or reconstructed major sources subject to a subsequently promulgated MACT standard or MACT requirement.

(a) If the Administrator promulgates an emission standard under section 112(d) or section 112(h) of the Act or the permitting authority issues a determination under section 112(j) of the Act that is applicable to a stationary source or group of sources which would be deemed to be a constructed or reconstructed major source under this subpart before the date that the owner or operator has obtained a final and legally effective MACT determination under any of the review options available pursuant to §63.43, the owner or operator of the source(s) shall comply with the promulgated standard or determination rather than any MACT determination under section 112(g) by the permitting authority, and the owner or operator shall comply with the promulgated standard by the compliance date in the promulgated standard.

(b) If the Administrator promulgates an emission standard under section 112(d) or section 112(h) of the Act or the permitting authority makes a determination under section 112(j) of the Act that is applicable to a stationary source or group of sources which was deemed to be a constructed or reconstructed major source under this subpart and has been subject to a prior case-by-case MACT determination pursuant to §63.43, and the owner and operator obtained a final and legally effective case-by-case MACT determination prior to the promulgation date of such emission standard, then the permitting authority shall (if the initial title V permit has not yet been issued) issue an initial operating permit which incorporates the emission standard or determination, or shall (if the initial title V permit has been issued) revise the operating permit according to the reopening procedures in 40 CFR part 70 or part 71, whichever is relevant, to incorporate the emission standard or determination.

(1) The EPA may include in the emission standard established under section 112(d) or section 112(h) of the Act a specific compliance date for those sources which have obtained a final and legally effective MACT determination under this subpart and which have submitted the information required by §63.43 to the EPA before the close of the public comment period for the standard established under section 112(d) of the Act. Such date shall assure that the owner or operator shall comply with the promulgated standard as expeditiously as practicable, but not longer than 8 years after such standard is promulgated. In that event, the permitting authority shall incorporate the applicable compliance date in the title V operating permit.

(2) If no compliance date has been established in the promulgated 112(d) or 112(h) standard or section 112(j) determination, for those sources which have obtained a final and legally effective MACT determination under this subpart, then the permitting authority shall establish a compliance date in the permit that assures that the owner or operator shall comply with the promulgated standard or determination as expeditiously as practicable, but not longer than 8 years after such standard is promulgated or a section 112(j) determination is made.

(c) Notwithstanding the requirements of paragraphs (a) and (b) of this section, if the Administrator promulgates an emission standard under section 112(d) or section 112(h) of the Act or the permitting authority issues a determination under section 112(j) of the Act that is applicable to a stationary source or group of sources which was deemed to be a constructed or reconstructed major source under this subpart and which is the subject of a prior case-by-case MACT determination pursuant to §63.43, and the level of control required by the emission standard issued under section 112(d) or section 112(h) or the determination issued under section 112(j) is less stringent than the level of control required by any emission limitation or standard in the prior MACT determination, the permitting authority is not required to incorporate any less stringent terms of the promulgated standard in the title V operating permit applicable to such source(s) and may in its discretion consider any more stringent provisions of the prior MACT determination to be applicable legal requirements when issuing or revising such an operating permit.

[61 FR 68404, Dec. 27, 1996]

§§ 63.45-63.49 [Reserved]

§ 63.50 Applicability.

(a) *General applicability.* (1) The requirements of this section through §63.56 implement section 112(j) of the Clean Air Act (as amended in 1990). The requirements of this section through §63.56 apply in each State beginning on the effective date of an approved title V permit program in such State. The requirements of this section through §63.56 do not apply to research or laboratory activities as defined in §63.51.

(2) The requirements of this section through §63.56 apply to:

(i) The owner or operator of affected sources within a source category or subcategory under this part that are located at a major source that is subject to an approved title V permit program and for which the Administrator has failed to promulgate emission standards by the section 112(j) deadlines. If title V applicability has been deferred for a source category, then section 112(j) is not applicable for sources in that category within that State, local or tribal jurisdiction until those sources become subject to title V permitting requirements; and

(ii) Permitting authorities with an approved title V permit program.

(b) Relationship to State and local requirements. Nothing in §§63.50 through 63.56 shall prevent a State or local regulatory agency from imposing more stringent requirements, as a matter of State or local law, than those contained in §§63.50 through 63.56.

(c) The procedures in §§63.50 through 63.56 apply for each affected source only after the section 112(j) deadline for the source category or subcategory in question has passed, and only until such time as a generally applicable Federal standard governing that source has been promulgated under section 112(d) or 112(h) of the Act. Once a generally applicable Federal standard governing that source has been promulgated, the owner or operator of the affected source and the permitting authority are not required to take any further actions to develop an equivalent emission limitation under section 112(j) of the Act.

(d) Any final equivalent emission limitation for an affected source which is issued by the permitting authority pursuant to §§63.50 through 63.56 prior to promulgation of a generally applicable Federal standard governing that source under section 112(d) or 112(h) of the Act shall be deemed an applicable Federal requirement adopted pursuant to section 112(j) of the Act. Each such equivalent emission limitation shall take effect upon issuance of the permit containing that limitation under section 112(j)(5) of the Act, and shall remain applicable to the source until such time as it may be revised or supplanted pursuant to the procedures established by §§63.50 through 63.56. Such a final equivalent emission limitation, and all associated requirements adopted pursuant to §63.52(f)(2), are directly enforceable under Federal law regardless of whether or not any permit in which they may be contained remains in effect.

[59 FR 26449, May 20, 1994, as amended at 67 FR 16605, Apr. 5, 2002; 68 FR 32601, May 30, 2003]

§ 63.51 Definitions.

Terms used in §§63.50 through 63.56 that are not defined in this section have the meaning given to them in the Act, or in subpart A of this part.

Affected source means the collection of equipment, activities, or both within a single contiguous area and under common control that is in a section 112(c) source category or subcategory for which the Administrator has failed to promulgate an emission standard by the section 112(j) deadline, and that is addressed by an applicable MACT emission limitation established pursuant to this subpart.

Available information means, for purposes of conducting a MACT floor finding and identifying control technology options under this subpart, any information that is available as of the date on which the first Part 2 MACT application is filed for a source in the relevant source category or subcategory in the State or jurisdiction; and, pursuant to the requirements of this subpart, is additional relevant information that can be expeditiously provided by the Administrator, is submitted by the applicant or others prior to or during the public comment period on the section 112(j) equivalent emission limitation for that source, or information contained in the information sources in paragraphs (1) through (5) of this definition.

(1) A relevant proposed regulation, including all supporting information;

(2) Relevant background information documents for a draft or proposed regulation.

(3) Any relevant regulation, information or guidance collected by the Administrator establishing a MACT floor finding and/or MACT determination.

(4) Relevant data and information available from the Clean Air Technology Center developed pursuant to section 112(l)(3) of the Act.

(5) Relevant data and information contained in the Aerometric Information Retrieval System (AIRS).

(6) Any additional information that can be expeditiously provided by the Administrator, and

(7) Any information provided by applicants in an application for a permit, permit modification, administrative amendment, or Notice of MACT Approval pursuant to the requirements of this subpart.

(8) Any additional relevant information provided by the applicant.

Control technology means measures, processes, methods, systems, or techniques to limit the emission of hazardous air pollutants including, but not limited to, measures which:

(1) Reduce the quantity, or eliminate emissions, of such pollutants through process changes, substitution of materials or other modifications;

(2) Enclose systems or processes to eliminate emissions;

(3) Collect, capture, or treat such pollutants when released from a process, stack, storage or fugitive emissions point;

(4) Are design, equipment, work practice, or operational standards (including requirements for operator training or certification) as provided in 42 U.S.C. 7412(h); or

(5) Are a combination of paragraphs (1) through (4) of this definition.

Enhanced review means a review process containing all administrative steps needed to ensure that the terms and conditions resulting from the review process can be incorporated using title V permitting procedures.

Equivalent emission limitation means an emission limitation, established under section 112(j) of the Act, which is equivalent to the MACT standard that EPA would have promulgated under section 112(d) or (h) of the Act.

Maximum achievable control technology (MACT) emission limitation for existing sources means the emission limitation reflecting the maximum degree of reduction in emissions of hazardous air pollutants (including a prohibition on such emissions, where achievable) that the Administrator, taking into consideration the cost of achieving such emission reductions, and any non-air quality health and environmental impacts and energy requirements, determines is achievable by sources in the category or subcategory to which such emission standard applies. This limitation shall not be less stringent than the MACT floor.

Maximum achievable control technology (MACT) emission limitation for new sources means the emission limitation which is not less stringent than the emission limitation achieved in practice by the best controlled similar source, and which reflects the maximum degree of reduction in emissions of hazardous air pollutants (including a prohibition on such emissions, where achievable) that the Administrator, taking into consideration the cost of achieving such emission reduction, and any non-air quality health and environmental impacts and energy requirements, determines is achievable by sources in the category or subcategory to which such emission standard applies.

Maximum Achievable Control Technology (MACT) floor means:

(1) For existing sources:

(i) The average emission limitation achieved by the best performing 12 percent of the existing sources in the United States (for which the Administrator has emissions information), excluding those sources that have, within 18 months before the emission standard is proposed or within 30 months before such standard is promulgated, whichever is later, first achieved a level of emission rate or emission reduction which complies, or would comply if the source is not subject to such standard, with the lowest achievable emission rate (as defined in section 171 of the Act) applicable to the source category and prevailing at the time, in the category or subcategory, for categories and subcategories of stationary sources with 30 or more sources; or

(ii) The average emission limitation achieved by the best performing five sources (for which the Administrator has or could reasonably obtain emissions information) in the category or subcategory, for categories or subcategories with fewer than 30 sources;

(2) For new sources, the emission limitation achieved in practice by the best controlled similar source.

New affected source means the collection of equipment, activities, or both, that if constructed after the issuance of a section 112(j) permit for the source pursuant to §63.52, is subject to the applicable MACT emission limitation for new sources. Each permit must define the term "new affected source," which will be the same as the "affected source" unless a different collection is warranted based on consideration of factors including:

(1) Emission reduction impacts of controlling individual sources versus groups of sources;

(2) Cost effectiveness of controlling individual equipment;

(3) Flexibility to accommodate common control strategies;

(4) Cost/benefits of emissions averaging;

(5) Incentives for pollution prevention;

(6) Feasibility and cost of controlling processes that share common equipment (*e.g.*, product recovery devices);

(7) Feasibility and cost of monitoring; and

(8) Other relevant factors.

Permitting authority means the permitting authority as defined in part 70 of this chapter.

Research or laboratory activities means activities whose primary purpose is to conduct research and development into new processes and products where such activities are operated under the close supervision of technically trained personnel and are not engaged in the manufacture of products for commercial sale in commerce, except in a de minimis manner; and where the source is not in a source category, specifically addressing research or laboratory activities, that is listed pursuant to section 112(c)(7) of the Act.

Section 112(j) deadline means the date 18 months after the date for which a relevant standard is scheduled to be promulgated under this part, except that for all major sources listed in the source category schedule for which a relevant standard is scheduled to be promulgated by November 15, 1994, the section 112(j) deadline is November 15, 1996, and for all major sources listed in the source category schedule for which a relevant standard is scheduled to be promulgated by November 15, 1997, the section 112(j) deadline is December 15, 1999.

Similar source means that equipment or collection of equipment that, by virtue of its structure, operability, type of emissions and volume and concentration of emissions, is substantially equivalent to the new affected source and employs control technology for control of emissions of hazardous air pollutants that is practical for use on the new affected source.

Source category schedule for standards means the schedule for promulgating MACT standards issued pursuant to section 112(e) of the Act.

[59 FR 26449, May 20, 1994, as amended at 61 FR 21372, May 10, 1996; 64 FR 26314, May 14, 1999; 67 FR 16605, Apr. 5, 2002]

§ 63.52 Approval process for new and existing affected sources.

(a) *Sources subject to section 112(j) as of the section 112(j) deadline.* The requirements of paragraphs (a)(1) and (2) of this section apply to major sources that include, as of the section 112(j) deadline, one or more sources in a category or subcategory for which the Administrator has failed to promulgate an emission standard under this part on or before an applicable section 112(j) deadline. Existing source MACT requirements (including relevant compliance deadlines), as specified in a title V permit issued to the source pursuant to the requirements of the subpart, must apply to such sources.

(1) The owner or operator must submit an application for a title V permit or for a revision to an existing title V permit or a pending title V permit meeting the requirements of §63.53(a) by the section 112(j) deadline if the owner or operator can reasonably determine that one or more sources at the major source belong in the category or subcategory subject to section 112(j).

(2) If an application was not submitted under paragraph (a)(1) of this section and if notified by the permitting authority, the owner or operator must submit an application for a title V permit or for a revision to an existing title V permit or a pending title V permit meeting the requirements of §63.53(a) within 30 days after being notified in writing by the permitting authority that one or more sources at the major source belong to such category or subcategory. Permitting authorities are not required to make such notification.

(3) The requirements in paragraphs (a)(3)(i) through (ii) of this section apply when the owner or operator has obtained a title V permit that incorporates a case-by-case MACT determination by the permitting authority under section 112(g) or has submitted a title V permit application for a revision that incorporates a case-by-case MACT determination under section 112(g), but has not submitted an application for a title V permit revision that addresses the emission limitation requirements of section 112(j).

(i) When the owner or operator has a title V permit that incorporates a case-by-case MACT determination by the permitting authority under section 112(g), the owner or operator must submit an application meeting the requirements of §63.53(a) for a title V permit revision within 30 days of the section 112(j) deadline or within 30 days of being notified in writing by the permitting authority that one or more sources at the major source belong in such category or subcategory. Using the procedures established in paragraph (e) of this section, the permitting authority must determine whether the emission limitations adopted pursuant to the prior case-by-case MACT determination under section 112(g) are substantially as effective as the emission limitations which the permitting authority would otherwise adopt pursuant to section 112(j) for the source in question. If the permitting authority determines that the emission limitations previously adopted to effectuate section 112(g) are substantially as effective as the emission limitations which the permitting authority would otherwise adopt to effectuate section 112(j) for the source, then the permitting authority must retain the existing emission limitations in the permit as the emission limitations to effectuate section 112(j). The title V permit applicable to that source must be revised accordingly. If the permitting authority does not retain the existing emission limitations in the permit as the emission limitations to effectuate section 112(j), the MACT requirements of this subpart are satisfied upon issuance of a revised title V permit incorporating any additional section 112(j) requirements.

(ii) When the owner or operator has submitted a title V permit application that incorporates a case-by-case MACT determination by the permitting authority under section 112(g), but has not received the permit incorporating the section 112(g) requirements, the owner or operator must continue to pursue a title V permit that addresses the emission limitation requirements of section 112(g). Within 30 days of issuance of that title V permit, the owner or operator must submit an application meeting the requirements of §63.53(a) for a change to the existing title V permit. Using the procedures established in paragraph (e) of this section, the permitting authority must determine whether the emission limitations adopted pursuant to the prior case-by-case MACT determination under section 112(g) are substantially as effective as the emission limitations which the permitting authority would otherwise adopt pursuant to section 112(j) for the source in question. If the permitting authority determines that the emission limitations previously adopted to effectuate section 112(g) are substantially as effective as the emission limitations which the permitting authority would otherwise adopt to effectuate section 112(j) for the source, then the permitting authority must retain the existing emission limitations in the permit as the emission limitations to effectuate section 112(j). The title V permit applicable to that source must be revised accordingly. If the permitting authority does not retain the existing emission limitations in the permit as the emission limitations to effectuate section 112(j), the MACT requirements of this subpart are satisfied upon issuance of a revised title V permit incorporating any additional section 112(j) requirements.

(b) *Sources that become subject to section 112(j) after the section 112(j) deadline and that do not have a title V permit addressing section 112(j) requirements.* The requirements of paragraphs (b)(1) through (4) of this section apply to sources that do not meet the criteria in paragraph (a) of this section on the section

112(j) deadline and are, therefore, not subject to section 112(j) on that date, but where events occur subsequent to the section 112(j) deadline that would bring the source under the requirements of this subpart, and the source does not have a title V permit that addresses the requirements of section 112(j).

(1) When one or more sources in a category or subcategory subject to the requirements of this subpart are installed at a major source, or result in the source becoming a major source due to the installation, and the installation does not invoke section 112(g) requirements, the owner or operator must submit an application meeting the requirements of §63.53(a) within 30 days of startup of the source. This application shall be reviewed using the procedures established in paragraph (e) of this section. Existing source MACT requirements (including relevant compliance deadlines), as specified in a title V permit issued pursuant to the requirements of this subpart, shall apply to such sources.

(2) The requirements in this paragraph apply when one or more sources in a category or subcategory subject to this subpart are installed at a major source, or result in the source becoming a major source due to the installation, and the installation does require emission limitations to be established and permitted under section 112(g), and the owner or operator has not submitted an application for a title V permit revision that addresses the emission limitation requirements of section 112(j). In this case, the owner or operator must apply for and obtain a title V permit that addresses the emission limitation requirements of section 112(g). Within 30 days of issuance of that title V permit, the owner or operator must submit an application meeting the requirements of §63.53(a) for a revision to the existing title V permit. Using the procedures established in paragraph (e) of this section, the permitting authority must determine whether the emission limitations adopted pursuant to the prior case-by-case MACT determination under section 112(g) are substantially as effective as the emission limitations which the permitting authority would otherwise adopt pursuant to section 112(j) for the source in question. If the permitting authority determines that the emission limitations previously adopted to effectuate section 112(g) are substantially as effective as the emission limitations which the permitting authority would otherwise adopt to effectuate section 112(j) for the source, then the permitting authority must retain the existing emission limitations in the permit as the emission limitations to effectuate section 112(j). The title V permit applicable to that source must be revised accordingly. If the permitting authority does not retain the existing emission limitations in the permit as the emission limitations to effectuate section 112(j), the MACT requirements of this subpart are satisfied upon issuance of a revised title V permit incorporating any additional section 112(j) requirements.

(3) The owner or operator of an area source that, due to a relaxation in any federally enforceable emission limitation (such as a restriction on hours of operation), increases its potential to emit hazardous air pollutants such that the source becomes a major source that is subject to this subpart, must submit an application meeting the requirements of §63.53(a) for a title V permit or for an application for a title V permit revision within 30 days after the date that such source becomes a major source. This application must be reviewed using the procedures established in paragraph (e) of this section. Existing source MACT requirements (including relevant compliance deadlines), as specified in a title V permit issued pursuant to the requirements of this subpart, must apply to such sources.

(4) On or after April 5, 2002, if the Administrator establishes a lesser quantity emission rate under section 112(a)(1) of the Act that results in an area source becoming a major source that is subject to this subpart, then the owner or operator of such a major source must submit an application meeting the requirements of §63.53(a) for a title V permit or for a change to an existing title V permit or pending title V permit on or before the date 6 months after the date that such source becomes a major source. Existing source MACT requirements (including relevant compliance deadlines), as specified in a title V permit issued pursuant to the requirements of this subpart, shall apply to such sources.

(c) *Sources that have a title V permit addressing section 112(j) requirements.* The requirements of paragraphs (c)(1) and (2) of this section apply to major sources that include one or more sources in a category or subcategory for which the Administrator fails to promulgate an emission standard under this part on or before an applicable section 112(j) deadline, and the owner or operator has a permit meeting the section 112(j) requirements, and where changes occur at the major source to equipment, activities, or both, subsequent to the section 112(j) deadline.

(1) If the title V permit already provides the appropriate requirements that address the events that occur under paragraph (c) of this section subsequent to the section 112(j) deadline, then the source must comply with the applicable new source MACT or existing source MACT requirements as specified in the permit, and the section 112(j) requirements are thus satisfied.

(2) If the title V permit does not contain the appropriate requirements that address the events that occur under paragraph (c) of this section subsequent to the section 112(j) deadline, then the owner or operator must submit an application for a revision to the existing title V permit that meets the requirements of §63.53(a). The application must be submitted within 30 days of beginning construction and must be reviewed using the procedures established in paragraph (e) of this section. Existing source MACT requirements (including relevant compliance deadlines), as specified in a title V permit issued pursuant to the requirements of this subpart, shall apply to such sources.

(d) *Requests for applicability determination or notice of MACT approval.* (1) An owner or operator who is unsure of whether one or more sources at a major source belong in a category or subcategory for which the Administrator has failed to promulgate an emission standard under this part may, on or before an applicable section 112(j) deadline, request an applicability determination from the permitting authority by submitting an application meeting the requirements of §63.53(a) by the applicable deadlines specified in paragraphs (a), (b), or (c) of this section.

(2) In addition to meeting the requirements of paragraphs (a), (b), and (c) of this section, the owner or operator of a new affected source may submit an application for a Notice of MACT Approval before construction, pursuant to §63.54.

(e) *Permit application review.* (1) Each owner or operator who is required to submit to the permitting authority a Part 1 MACT application which meets the requirements of §63.53(a) for one or more sources in a category or subcategory subject to section 112(j) must also submit to the permitting authority a timely Part 2 MACT application for the same sources which meets the requirements of §63.53(b). Each owner or operator shall submit the Part 2 MACT application for the sources in a particular category or subcategory no later than the applicable date specified in Table 1 to this subpart. The submission date specified in Table 1 to this subpart for Miscellaneous Organic Chemical Manufacturing shall apply to sources in each of the source categories listed in Table 2 to this subpart. When the owner or operator is required by §§63.50 through 63.56 to submit an application meeting the requirements of §63.53(a) by a date which is after the date for a Part 2 MACT application for sources in the category or subcategory in question established by Table 1 to this subpart, the owner or operator shall submit a Part 2 MACT application meeting the requirements of §63.53(b) within 60 additional days after the applicable deadline for submission of the Part 1 MACT application. Part 2 MACT applications must be reviewed by the permitting authority according to procedures established in §63.55. The resulting MACT determination must be incorporated into the source's title V permit according to procedures established under title V, and any other regulations approved under title V in the jurisdiction in which the affected source is located.

(2) Notwithstanding paragraph (e)(1) of this section, the owner or operator may request either an applicability determination or an equivalency determination by the permitting authority as provided in paragraphs (e)(2)(i) and (ii) of this section.

(i) Each owner or operator who submitted a request for an applicability determination pursuant to paragraph (d)(1) of this section on or before May 15, 2002, which remains pending before the permitting authority on May 30, 2003, and who still wishes to obtain such a determination, must resubmit that request by July 29, 2003, or by the date which is 60 days after the Administrator publishes in theFederal Registera proposed standard under section 112(d) or 112(h) of the Act for the category or subcategory in question, whichever is later. Each request for an applicability determination which is resubmitted under this paragraph (e)(2)(i) must be supplemented to discuss the relation between the source(s) in question and the applicability provision in the proposed standard for the category or subcategory in question, and to explain why there may still be uncertainties that require a determination of applicability. The permitting authority must take action upon each properly resubmitted and supplemented request for an applicability determination within an additional 60 days after the applicable deadline for the resubmitted request. If the applicability determination is positive, the owner or operator must submit a Part 2 MACT application meeting the requirements of §63.53(b) by the date specified for the category or subcategory in question in Table 1 to this subpart. If the applicability determination is negative, then no further action by the owner or operator is necessary.

(ii) As specified in paragraphs (a) and (b) of this section, an owner or operator who has submitted an application meeting the requirements of §63.53(a) may request a determination by the permitting authority of whether emission limitations adopted pursuant to a prior case-by-case MACT determination under section 112(g) that apply to one or more sources at a major source in a relevant category or subcategory are substantially as effective as the emission limitations which the permitting authority would otherwise adopt pursuant to section 112(j) for the source in question. Such a request must be submitted by the date for the category or subcategory in question specified in Table 1 to this subpart. Any owner or operator who previously submitted such a request under a prior version of this paragraph (e)(2)(ii) need not resubmit the request. Each request for an equivalency determination under this paragraph (e)(2)(ii), regardless of when it was submitted, will be construed in the alternative as a complete application for an equivalent emission limitation under section 112(j). The process for determination by the permitting authority of whether the emission limitations in the prior case-by-case MACT determination are substantially as effective as the emission limitations which the permitting authority would otherwise adopt under section 112(j) must include the opportunity for full public, EPA, and affected State review prior to a final determination. If the permitting authority determines that the emission limitations in the prior case-by-case MACT determination are substantially as effective as the emission limitations which the permitting authority would otherwise adopt under section 112(j), then the permitting authority must adopt the existing emission limitations in the permit as the emission limitations to effectuate section 112(j) for the source in question. If more than 3 years remain on the current title V permit, the owner or operator must submit an application for a title V permit revision to make any conforming changes in the permit required to adopt the existing emission limitations as the section 112(j) MACT emission limitations. If less than 3 years remain on the current title V permit, any required conforming changes must be made when the permit is renewed. If the permitting authority determines that the emission limitations in the prior case-by-case MACT determination under section 112(g) are not substantially as effective as the emission limitations which the permitting authority would otherwise adopt for the source in question under section 112(j), the permitting authority must make a new MACT determination and adopt a title V permit incorporating an appropriate equivalent emission limitation under section 112(j). Such a determination constitutes final action for purposes of judicial review under 40 CFR 70.4(b)(3)(x) and corresponding State title V program provisions.

(3) Within 60 days of submittal of the Part 2 MACT application, the permitting authority must notify the owner or operator in writing whether the application is complete or incomplete. The Part 2 MACT application shall be deemed complete on the date it was submitted unless the permitting authority notifies the owner or operator in writing within 60 days of the submittal that the Part 2 MACT application is incomplete. A Part 2 MACT application is complete if it is sufficient to begin processing the application for a title V permit addressing section 112(j) requirements. In the event that the permitting authority disapproves a permit application or determines that the application is incomplete, the owner or operator must revise and resubmit the application to meet the objections of the permitting authority. The permitting authority must specify a reasonable period in which the owner or operator is required to remedy the deficiencies in the disapproved or incomplete application. This period may not exceed 6 months from the date the owner or operator is first notified that the application has been disapproved or is incomplete.

(4) Following submittal of a Part 1 or Part 2 MACT application, the permitting authority may request additional information from the owner or operator. The owner or operator must respond to such requests in a timely manner.

(5) If the owner or operator has submitted a timely and complete application as required by this section, any failure to have a title V permit addressing section 112(j) requirements shall not be a violation of section 112(j), unless the delay in final action is due to the failure of the applicant to submit, in a timely manner, information required or requested to process the application. Once a complete application is submitted, the owner or operator shall not be in violation of the requirement to have a title V permit addressing section 112(j) requirements.

(f) *Permit content.* The title V permit must contain an equivalent emission limitation (or limitations) for the relevant category or subcategory determined on a case-by-case basis by the permitting authority, or, if the applicable criteria in subpart D of this part are met, the title V permit may contain an alternative emission limitation. For the purposes of the preceding sentence, early reductions made pursuant to section 112(i)(5)(A) of the Act must be achieved not later than the date on which the relevant standard should have been promulgated according to the source category schedule for standards.

(1) The title V permit must contain an emission standard or emission limitation that is equivalent to existing source MACT and an emission standard or emission limitation that is equivalent to new source MACT for control of emissions of hazardous air pollutants. The MACT emission standards or limitations must be determined by the permitting authority and must be based on the degree of emission reductions that can be achieved if the control technologies or work practices are installed, maintained, and operated properly. The permit must also specify the affected source and the new affected source. If construction of a new affected

source or reconstruction of an affected source commences after a title V permit meeting the requirements of section 112(j) has been issued for the source, the new source MACT compliance dates must apply.

(2) The title V permit must specify any notification, operation and maintenance, performance testing, monitoring, and reporting and recordkeeping requirements. In developing the title V permit, the permitting authority must consider and specify the appropriate provisions of subpart A of this part. The title V permit must also include the information in paragraphs (f)(2)(i) through (iii) of this section.

(i) In addition to the MACT emission limitation required by paragraph (f)(1) of this section, additional emission limits, production limits, operational limits or other terms and conditions necessary to ensure practicable enforceability of the MACT emission limitation.

(ii) Compliance certifications, testing, monitoring, reporting and recordkeeping requirements that are consistent with requirements established pursuant to title V and paragraph (h) of this section.

(iii) Compliance dates by which the owner or operator must be in compliance with the MACT emission limitation and all other applicable terms and conditions of the permit.

(A) The owner or operator of an affected source subject to the requirements of this subpart must comply with the emission limitation(s) by the date established in the source's title V permit. In no case shall such compliance date be later than 3 years after the issuance of the permit for that source, except where the permitting authority issues a permit that grants an additional year to comply in accordance with section 112(i)(3)(B) of the Act, or unless otherwise specified in section 112(i), or in subpart D of this part.

(B) The owner or operator of a new affected source, as defined in the title V permit meeting the requirements of section 112(j), that is subject to the requirements of this subpart must comply with a new source MACT level of control immediately upon startup of the new affected source.

(g) *Permit issuance dates.* The permitting authority must issue a title V permit meeting section 112(j) requirements within 18 months after submittal of the complete Part 2 MACT application.

(h) *Enhanced monitoring.* In accordance with section 114(a)(3) of the Act, monitoring shall be capable of demonstrating continuous compliance for each compliance period during the applicable reporting period. Such monitoring data shall be of sufficient quality to be used as a basis for directly enforcing all applicable requirements established under this subpart, including emission limitations.

(i) *MACT emission limitations.* (1) The owner or operator of affected sources subject to paragraphs (a), (b), and (c) of this section must comply with all requirements of this subpart that are applicable to affected sources, including the compliance date for affected sources established in paragraph (f)(2)(iii)(A) of this section.

(2) The owner or operator of new affected sources subject to paragraph (c)(1) of this section must comply with all requirements of this subpart that are applicable to new affected sources, including the compliance date for new affected sources established in paragraph (f)(2)(iii)(B) of this section.

[67 FR 16606, Apr. 5, 2002; 68 FR 32602, May 30, 2003]

§ 63.53 Application content for case-by-case MACT determinations.

(a) *Part 1 MACT application.* The Part 1 application for a MACT determination must contain the information in paragraphs (a)(1) through (4) of this section.

(1) The name and address (physical location) of the major source.

(2) A brief description of the major source and an identification of the relevant source category.

(3) An identification of the types of emission points belonging to the relevant source category.

(4) An identification of any affected sources for which a section 112(g) MACT determination has been made.

(b) *Part 2 MACT application.* (1) In compiling a Part 2 MACT application, the owner or operator may cross-reference specific information in any prior submission by the owner or operator to the permitting authority, but in cross-referencing such information the owner or operator may not presume favorable action on any prior application or request which is still pending. In compiling a Part 2 MACT application, the owner or operator may also cross-reference any part of a standard proposed by the Administrator pursuant to section 112(d) or 112(h) of the Act for any category or subcategory which includes sources to which the Part 2 application applies.

(2) The Part 2 application for a MACT determination must contain the information in paragraphs (b)(2)(i) through (b)(2)(v) of this section.

(i) For a new affected source, the anticipated date of startup of operation.

(ii) Each emission point or group of emission points at the affected source which is part of a category or subcategory for which a Part 2 MACT application is required, and each of the hazardous air pollutants emitted at those emission points. When the Administrator has proposed a standard pursuant to section 112(d) or 112(h) of the Act for a category or subcategory, such information may be limited to those emission points and hazardous air pollutants which would be subject to control under the proposed standard.

(iii) Any existing Federal, State, or local limitations or requirements governing emissions of hazardous air pollutants from those emission points which are part of a category or subcategory for which a Part 2 application is required.

(iv) For each identified emission point or group of affected emission points, an identification of control technology in place.

(v) Any additional emission data or other information specifically requested by the permitting authority.

(3) The Part 2 application for a MACT determination may, but is not required to, contain the following information:

(i) Recommended emission limitations for the affected source and support information consistent with §63.52(f). The owner or operator may recommend a specific design, equipment, work practice, or operational standard, or combination thereof, as an emission limitation.

(ii) A description of the control technologies that would be applied to meet the emission limitation including technical information on the design, operation, size, estimated control efficiency and any other information deemed appropriate by the permitting authority, and identification of the affected sources to which the control technologies must be applied.

(iii) Relevant parameters to be monitored and frequency of monitoring to demonstrate continuous compliance with the MACT emission limitation over the applicable reporting period.

[67 FR 16609, Apr. 5, 2002, as amended at 68 FR 32602, May 30, 2003]

§ 63.54 Preconstruction review procedures for new affected sources.

The requirements of this section apply to an owner or operator who constructs a new affected source subject to §63.52(c)(1). The purpose of this section is to describe alternative review processes that the permitting authority may use to make a MACT determination for the new affected source.

(a) *Review process for new affected sources.* (1) If the permitting authority requires an owner or operator to obtain or revise a title V permit before construction of the new affected source, or when the owner or operator chooses to obtain or revise a title V permit before construction, the owner or operator must follow the procedures established under the applicable title V permit program before construction of the new affected source.

(2) If an owner or operator is not required to obtain or revise a title V permit before construction of the new affected source (and has not elected to do so), but the new affected source is covered by any preconstruction or preoperation review requirements established pursuant to section 112(g) of the Act, then the owner or operator must comply with those requirements in order to ensure that the requirements of section 112(j) and (g) are satisfied. If the new affected source is not covered by section 112(g), the permitting authority, in its discretion, may issue a Notice of MACT Approval, or the equivalent, in accordance with the procedures set forth in paragraphs (b) through (f) of this section, or an equivalent permit review process, before construction or operation of the new affected source.

(3) Regardless of the review process, the MACT determination shall be consistent with the principles established in §63.55. The application for a Notice of MACT Approval or a title V permit, permit modification, or administrative amendment, whichever is applicable, shall include the documentation required by §63.53.

(b) *Optional administrative procedures for preconstruction or preoperation review for new affected sources.* The permitting authority may provide for an enhanced review of section 112(j) MACT determinations for review procedures and compliance requirements equivalent to those set forth in paragraphs (b) through (f) of this section.

(1) The permitting authority will notify the owner or operator in writing as to whether the application for a MACT determination is complete or whether additional information is required.

(2) The permitting authority will approve an applicant's proposed control technology, or the permitting authority will notify the owner or operator in writing of its intention to disapprove a control technology.

(3) The owner or operator may present in writing, within a time frame specified by the permitting authority, additional information, considerations, or amendments to the application before the permitting authority's issuance of a final disapproval.

(4) The permitting authority will issue a preliminary approval or issue a disapproval of the application, taking into account additional information received from the owner or operator.

(5) A determination to disapprove any application will be in writing and will specify the grounds on which the disapproval is based.

(6) Approval of an applicant's proposed control technology must be set forth in a Notice of MACT Approval (or the equivalent) as described in §63.52(f).

(c) *Opportunity for public comment on Notice of MACT Approval.* The permitting authority will provide opportunity for public comment on the preliminary Notice of MACT Approval prior to issuance, including, at a minimum,.

(1) Availability for public inspection in at least one location in the area affected of the information submitted by the owner or operator and of the permitting authority's tentative determination;

(2) A period for submittal of public comment of at least 30 days; and

(3) A notice by prominent advertisement in the area affected of the location of the source information and analysis specified in §63.52(f). The form and content of the notice must be substantially equivalent to that found in §70.7 of this chapter.

(4) An opportunity for a public hearing, if one is requested. The permitting authority will give at least 30 days notice in advance of any hearing.

(d) *Review by the EPA and affected States.* The permitting authority must send copies of the preliminary notice (in time for comment) and final notice required by paragraph (c) of this section to the Administrator through the appropriate Regional Office, and to all other State and local air pollution control agencies having jurisdiction in affected States. The permitting authority must provide EPA with a review period for the final notice of at least 45 days and shall not issue a final Notice of MACT Approval until EPA objections are satisfied.

(e) *Compliance with MACT determinations.* An owner or operator of a major source that is subject to a MACT determination must comply with notification, operation and maintenance, performance testing, monitoring, reporting, and recordkeeping requirements established under §63.52(h), under title V, and at the discretion of the permitting authority, under subpart A of this part. The permitting authority must provide the EPA with the opportunity to review compliance requirements for consistency with requirements established pursuant to title V during the review period under paragraph (d) of this section.

(f) *Equivalency under section 112(l).* If a permitting authority requires preconstruction review for new source MACT determinations under this subpart, such requirement shall not necessitate a determination under subpart E of this part.

[59 FR 26449, May 20, 1994, as amended at 67 FR 16610, Apr. 5, 2002]

§ 63.55 Maximum achievable control technology (MACT) determinations for affected sources subject to case-by-case determination of equivalent emission limitations.

(a) *Requirements for permitting authorities.* The permitting authority must determine whether the §63.53(a) Part 1 and §63.53(b) Part 2 MACT application is complete or an application for a Notice of MACT Approval is approvable. In either case, when the application is complete or approvable, the permitting authority must establish hazardous air pollutant emissions limitations equivalent to the limitations that would apply if an emission standard had been issued in a timely manner under section 112(d) or (h) of the Act. The permitting authority must establish these emissions limitations consistent with the following requirements and principles:

(1) Emission limitations must be established for the equipment and activities within the affected sources within a source category or subcategory for which the section 112(j) deadline has passed.

(2) Each emission limitation for an existing affected source must reflect the maximum degree of reduction in emissions of hazardous air pollutants (including a prohibition on such emissions, where achievable) that the permitting authority, taking into consideration the cost of achieving such emission reduction and any non-air quality health and environmental impacts and energy requirements, determines is achievable by affected sources in the category or subcategory for which the section 112(j) deadline has passed. This limitation must not be less stringent than the MACT floor which must be established by the permitting authority according to the requirements of section 112(d)(3)(A) and (B) and must be based upon available information.

(3) Each emission limitation for a new affected source must reflect the maximum degree of reduction in emissions of hazardous air pollutants (including a prohibition on such emissions, where achievable) that the permitting authority, taking into consideration the cost of achieving such emission reduction and any non-air quality health and environmental impacts and energy requirements, determines is achievable. This limitation must not be less stringent than the emission limitation achieved in practice by the best controlled similar source which must be established by the permitting authority according to the requirements of section 112(d)(3). This limitation must be based upon available information.

(4) The permitting authority must select a specific design, equipment, work practice, or operational standard, or combination thereof, when it is not feasible to prescribe or enforce an equivalent emission limitation due to the nature of the process or pollutant. It is not feasible to prescribe or enforce a limitation when the Administrator determines that hazardous air pollutants cannot be emitted through a conveyance designed

and constructed to capture such pollutant, or that any requirement for, or use of, such a conveyance would be inconsistent with any Federal, State, or local law, or the application of measurement methodology to a particular class of sources is not practicable due to technological and economic limitations.

(5) Nothing in this subpart shall prevent a State or local permitting authority from establishing an emission limitation more stringent than required by Federal regulations.

(b) *Reporting to EPA.* The owner or operator must submit additional copies of its Part 1 and Part 2 MACT application for a title V permit, permit revision, or Notice of MACT Approval, whichever is applicable, to the EPA at the same time the material is submitted to the permitting authority.

[67 FR 16610, Apr. 5, 2002]

§ 63.56 Requirements for case-by-case determination of equivalent emission limitations after promulgation of subsequent MACT standard.

(a) If the Administrator promulgates a relevant emission standard that is applicable to one or more affected sources within a major source before the date a permit application under this paragraph (a) is approved, the title V permit must contain the promulgated standard rather than the emission limitation determined under §63.52, and the owner or operator must comply with the promulgated standard by the compliance date in the promulgated standard.

(b) If the Administrator promulgates a relevant emission standard under section 112(d) or (h) of the Act that is applicable to a source after the date a permit is issued pursuant to §63.52 or §63.54, the permitting authority must incorporate requirements of that standard in the title V permit upon its next renewal. The permitting authority must establish a compliance date in the revised permit that assures that the owner or operator must comply with the promulgated standard within a reasonable time, but not longer than 8 years after such standard is promulgated or 8 years after the date by which the owner or operator was first required to comply with the emission limitation established by the permit, whichever is earlier. However, in no event shall the period for compliance for existing sources be shorter than that provided for existing sources in the promulgated standard.

(c) Notwithstanding the requirements of paragraph (a) or (b) of this section, the requirements of paragraphs (c)(1) and (2) of this section shall apply.

(1) If the Administrator promulgates an emission standard under section 112(d) or (h) that is applicable to an affected source after the date a permit application under this paragraph is approved under §63.52 or §63.54, the permitting authority is not required to change the emission limitation in the permit to reflect the promulgated standard if the permitting authority determines that the level of control required by the emission limitation in the permit is substantially as effective as that required by the promulgated standard pursuant to §63.1(e).

(2) If the Administrator promulgates an emission standard under section 112(d) or (h) of the Act that is applicable to an affected source after the date a permit application is approved under §63.52 or §63.54, and the level of control required by the promulgated standard is less stringent than the level of control required by any emission limitation in the prior MACT determination, the permitting authority is not required to incorporate any less stringent emission limitation of the promulgated standard in the title V permit and may in its discretion consider any more stringent provisions of the MACT determination to be applicable legal requirements when issuing or revising such a title V permit.

Table 1 to Subpart B of Part 63—Section112(j)Part 2 Application Due Dates

Due date	MACT standard
10/30/03	Combustion Turbines.

	Lime Manufacturing. Site Remediation. Iron and Steel Foundries. Taconite Iron Ore Processing. Miscellaneous Organic Chemical Manufacturing (MON).[1]
	Organic Liquids Distribution. Primary Magnesium Refining. Metal Can (Surface Coating). Plastic Parts and Products (Surface Coating). Chlorine Production. Miscellaneous Metal Parts and Products (Surface Coating) (and Asphalt/Coal Tar Application—Metal Pipes).[2]
4/28/04	Industrial Boilers, Institutional/Commercial Boilers and Process Heaters.[3] Plywood and Composite Wood Products. Reciprocating Internal Combustion Engines.[4] Auto and Light-Duty Truck (Surface Coating).
11/14/05	Industrial Boilers, Institutional/Commercial Boilers, and Process Heaters.[5] Hydrochloric Acid Production.[6]

[1] Covers 23 source categories, see Table 2 to this subpart.

[2] Two source categories.

[3] Includes all sources in the three categories, Industrial Boilers, Institutional/Commercial Boilers, and Process Heaters that burn no hazardous waste.

[4] Includes engines greater than 500 brake horsepower.

[5] Includes all sources in the three categories, Industrial Boilers, Institutional/Commercial Boilers, and Process Heaters that burn hazardous waste.

[6] Includes furnaces that produce acid from hazardous waste at sources in the category Hydrochloric Acid Production.

[68 FR 32603, May 30, 2003, as amended at 70 FR 39664, July 11, 2005]

Table 2 to Subpart B of Part 63—MON Source Categories

Manufacture of Paints, Coatings, and Adhesives.

Alkyd Resins Production.

Maleic Anhydride Copolymers Production.

Polyester Resins Production.

Polymerized Vinylidene Chloride Production.

Polymethyl Methacrylate Resins Production.

Polyvinyl Acetate Emulsions Production.

Polyvinyl Alcohol Production.

Polyvinyl Butyral Production.

Ammonium Sulfate Production-Caprolactam By-Product Plants.

Quaternary Ammonium Compounds Production.

Benzyltrimethylammonium Chloride Production.

Carbonyl Sulfide Production.

Chelating Agents Production.

Chlorinated Paraffins Production.

Ethylidene Norbornene Production.

Explosives Production.

Hydrazine Production.

OBPA/1,3-Diisocyanate Production.

Photographic Chemicals Production.

Phthalate Plasticizers Production.

Rubber Chemicals Manufacturing.

Symmetrical Tetrachloropyridine Production.

[68 FR 32603, May 30, 2003]

Subpart Da—Standards of Performance for Electric Utility Steam Generating Units for Which Construction is Commenced After September 18, 1978

Source: 72 FR 32722, June 13, 2007, unless otherwise noted.

§ 60.40Da Applicability and designation of affected facility.

(a) The affected facility to which this subpart applies is each electric utility steam generating unit:

(1) That is capable of combusting more than 73 megawatts (MW) (250 million British thermal units per hour (MMBtu/hr) heat input of fossil fuel (either alone or in combination with any other fuel); and

(2) For which construction, modification, or reconstruction is commenced after September 18, 1978.

(b) Combined cycle gas turbines (both the stationary combustion turbine and any associated duct burners) are subject to this part and not subject to subpart GG or KKKK of this part if:

(1) The combined cycle gas turbine is capable of combusting more than 73 MW (250 MMBtu/hr) heat input of fossil fuel (either alone or in combination with any other fuel); and

(2) The combined cycle gas turbine is designed and intended to burn fuels containing 50 percent (by heat input) or more solid-derived fuel not meeting the definition of natural gas on a 12-month rolling average basis; and

(3) The combined cycle gas turbine commenced construction, modification, or reconstruction after February 28, 2005.

(4) This subpart will continue to apply to all other electric utility combined cycle gas turbines that are capable of combusting more than 73 MW (250 MMBtu/hr) heat input of fossil fuel in the heat recovery steam generator. If the heat recovery steam generator is subject to this subpart and the stationary combustion turbine is subject to either subpart GG or KKKK of this part, only emissions resulting from combustion of fuels in the steam-generating unit are subject to this subpart. (The stationary combustion turbine emissions are subject to subpart GG or KKKK, as applicable, of this part).

(c) Any change to an existing fossil-fuel-fired steam generating unit to accommodate the use of combustible materials, other than fossil fuels, shall not bring that unit under the applicability of this subpart.

(d) Any change to an existing steam generating unit originally designed to fire gaseous or liquid fossil fuels, to accommodate the use of any other fuel (fossil or nonfossil) shall not bring that unit under the applicability of this subpart.

§ 60.41Da Definitions.

As used in this subpart, all terms not defined herein shall have the meaning given them in the Act and in subpart A of this part.

Anthracite means coal that is classified as anthracite according to the American Society of Testing and Materials in ASTM D388 (incorporated by reference, see §60.17).

Available purchase power means the lesser of the following:

(a) The sum of available system capacity in all neighboring companies.

(b) The sum of the rated capacities of the power interconnection devices between the principal company and all neighboring companies, minus the sum of the electric power load on these interconnections.

(c) The rated capacity of the power transmission lines between the power interconnection devices and the electric generating units (the unit in the principal company that has the malfunctioning flue gas desulfurization system and the unit(s) in the neighboring company supplying replacement electrical power) less the electric power load on these transmission lines.

Available system capacity means the capacity determined by subtracting the system load and the system emergency reserves from the net system capacity.

Biomass means plant materials and animal waste.

Bituminous coal means coal that is classified as bituminous according to the American Society of Testing and Materials in ASTM D388 (incorporated by reference, see §60.17).

Boiler operating day for units constructed, reconstructed, or modified on or before February 28, 2005, means a 24-hour period during which fossil fuel is combusted in a steam-generating unit for the entire 24 hours. For units constructed, reconstructed, or modified after February 28, 2005, *boiler operating day* means a 24-hour period between 12 midnight and the following midnight during which any fuel is combusted at any time in the steam-generating unit. It is not necessary for fuel to be combusted the entire 24-hour period.

Coal means all solid fuels classified as anthracite, bituminous, subbituminous, or lignite by the American Society of Testing and Materials in ASTM D388 (incorporated by reference, see §60.17) and coal refuse. Synthetic fuels derived from coal for the purpose of creating useful heat, including but not limited to solvent-refined coal, gasified coal (not meeting the definition of natural gas), coal-oil mixtures, and coal-water mixtures are included in this definition for the purposes of this subpart.

Coal-fired electric utility steam generating unit means an electric utility steam generating unit that burns coal, coal refuse, or a synthetic gas derived from coal either exclusively, in any combination together, or in any combination with other fuels in any amount.

Coal refuse means waste products of coal mining, physical coal cleaning, and coal preparation operations (*e.g.* culm, gob, etc.) containing coal, matrix material, clay, and other organic and inorganic material.

Cogeneration, also known as "combined heat and power," means a steam-generating unit that simultaneously produces both electric (or mechanical) and useful thermal energy from the same primary energy source.

Combined cycle gas turbine means a stationary turbine combustion system where heat from the turbine exhaust gases is recovered by a steam generating unit.

Dry flue gas desulfurization technology or *dry FGD* means a sulfur dioxide control system that is located downstream of the steam generating unit and removes sulfur oxides (SO_2) from the combustion gases of the steam generating unit by contacting the combustion gases with an alkaline reagent and water, whether introduced separately or as a premixed slurry or solution and forming a dry powder material. This definition includes devices where the dry powder material is subsequently converted to another form. Alkaline slurries or solutions used in dry FGD technology include, but are not limited to, lime and sodium.

Duct burner means a device that combusts fuel and that is placed in the exhaust duct from another source, such as a stationary gas turbine, internal combustion engine, kiln, etc., to allow the firing of additional fuel to heat the exhaust gases before the exhaust gases enter a heat recovery steam generating unit.

Electric utility combined cycle gas turbine means any combined cycle gas turbine used for electric generation that is constructed for the purpose of supplying more than one-third of its potential electric output capacity and more than 25 MW net-electrical output to any utility power distribution system for sale. Any steam distribution system that is constructed for the purpose of providing steam to a steam electric generator that would produce electrical power for sale is also considered in determining the electrical energy output capacity of the affected facility.

Electric utility company means the largest interconnected organization, business, or governmental entity that generates electric power for sale (*e.g.* , a holding company with operating subsidiary companies).

Electric utility steam-generating unit means any steam electric generating unit that is constructed for the purpose of supplying more than one-third of its potential electric output capacity and more than 25 MW net-electrical output to any utility power distribution system for sale. Also, any steam supplied to a steam distribution system for the purpose of providing steam to a steam-electric generator that would produce electrical energy for sale is considered in determining the electrical energy output capacity of the affected facility.

Electrostatic precipitator or *ESP* means an add-on air pollution control device used to capture particulate matter (PM) by charging the particles using an electrostatic field, collecting the particles using a grounded collecting surface, and transporting the particles into a hopper.

Emergency condition means that period of time when:

(1) The electric generation output of an affected facility with a malfunctioning flue gas desulfurization system cannot be reduced or electrical output must be increased because:

(i) All available system capacity in the principal company interconnected with the affected facility is being operated, and

(ii) All available purchase power interconnected with the affected facility is being obtained, or

(2) The electric generation demand is being shifted as quickly as possible from an affected facility with a malfunctioning flue gas desulfurization system to one or more electrical generating units held in reserve by the principal company or by a neighboring company, or

(3) An affected facility with a malfunctioning flue gas desulfurization system becomes the only available unit to maintain a part or all of the principal company's system emergency reserves and the unit is operated in spinning reserve at the lowest practical electric generation load consistent with not causing significant physical damage to the unit. If the unit is operated at a higher load to meet load demand, an emergency condition would not exist unless the conditions under paragraph (1) of this definition apply.

Emission limitation means any emissions limit or operating limit.

Emission rate period means any calendar month included in a 12-month rolling average period.

Federally enforceable means all limitations and conditions that are enforceable by the Administrator, including the requirements of 40 CFR parts 60 and 61, requirements within any applicable State implementation plan, and any permit requirements established under 40 CFR 52.21 or under 40 CFR 51.18 and 51.24.

Fossil fuel means natural gas, petroleum, coal, and any form of solid, liquid, or gaseous fuel derived from such material for the purpose of creating useful heat.

Gaseous fuel means any fuel derived from coal or petroleum that is present as a gas at standard conditions and includes, but is not limited to, refinery fuel gas, process gas, coke-oven gas, synthetic gas, and gasified coal.

Gross output means the gross useful work performed by the steam generated and, for an IGCC electric utility steam generating unit, the fuel burned in stationary combustion turbines. For a unit generating only electricity, the gross useful work performed is the gross electrical output from the unit's turbine/generator sets. For a cogeneration unit, the gross useful work performed is the gross electrical or mechanical output plus 75 percent of the useful thermal output measured relative to ISO conditions that is not used to generate additional electrical or mechanical output (i.e., steam delivered to an industrial process).

24-hour period means the period of time between 12:01 a.m. and 12:00 midnight.

Integrated gasification combined cycle electric utility steam generating unit or *IGCC electric utility steam generating unit* means a coal-fired electric utility steam generating unit that burns a synthetic gas derived from coal in a combined-cycle gas turbine. No coal is directly burned in the unit during operation.

Interconnected means that two or more electric generating units are electrically tied together by a network of power transmission lines, and other power transmission equipment.

ISO conditions means a temperature of 288 Kelvin, a relative humidity of 60 percent, and a pressure of 101.3 kilopascals.

Lignite means coal that is classified as lignite A or B according to the American Society of Testing and Materials in ASTM D388 (incorporated by reference, see §60.17).

Natural gas means:

(1) A naturally occurring mixture of hydrocarbon and nonhydrocarbon gases found in geologic formations beneath the earth's surface, of which the principal constituent is methane; or

(2) Liquid petroleum gas, as defined by the American Society of Testing and Materials in ASTM D1835 (incorporated by reference, see §60.17); or

(3) A mixture of hydrocarbons that maintains a gaseous state at ISO conditions. Additionally, natural gas must either be composed of at least 70 percent methane by volume or have a gross calorific value between 34 and 43 megajoules (MJ) per standard cubic meter (910 and 1,150 Btu per standard cubic foot).

Neighboring company means any one of those electric utility companies with one or more electric power interconnections to the principal company and which have geographically adjoining service areas.

Net-electric output means the gross electric sales to the utility power distribution system minus purchased power on a calendar year basis.

Net system capacity means the sum of the net electric generating capability (not necessarily equal to rated capacity) of all electric generating equipment owned by an electric utility company (including steam generating units, internal combustion engines, gas turbines, nuclear units, hydroelectric units, and all other electric generating equipment) plus firm contractual purchases that are interconnected to the affected facility that has the malfunctioning flue gas desulfurization system. The electric generating capability of equipment under multiple ownership is prorated based on ownership unless the proportional entitlement to electric output is otherwise established by contractual arrangement.

Noncontinental area means the State of Hawaii, the Virgin Islands, Guam, American Samoa, the Commonwealth of Puerto Rico, or the Northern Mariana Islands.

Petroleum means crude oil or petroleum or a fuel derived from crude oil or petroleum, including, but not limited to, distillate oil, residual oil, and petroleum coke.

Potential combustion concentration means the theoretical emissions (nanograms per joule (ng/J), lb/MMBtu heat input) that would result from combustion of a fuel in an uncleaned state without emission control systems) and:

(1) For particulate matter (PM) is:

(i) 3,000 ng/J (7.0 lb/MMBtu) heat input for solid fuel; and

(ii) 73 ng/J (0.17 lb/MMBtu) heat input for liquid fuels.

(2) For sulfur dioxide (SO_2) is determined under §60.50Da(c).

(3) For nitrogen oxides (NO_X) is:

(i) 290 ng/J (0.67 lb/MMBtu) heat input for gaseous fuels;

(ii) 310 ng/J (0.72 lb/MMBtu) heat input for liquid fuels; and

(iii) 990 ng/J (2.30 lb/MMBtu) heat input for solid fuels.

Potential electrical output capacity means 33 percent of the maximum design heat input capacity of the steam generating unit, divided by 3,413 Btu/KWh, divided by 1,000 kWh/MWh, and multiplied by 8,760 hr/yr (*e.g.* , a steam generating unit with a 100 MW (340 MMBtu/hr) fossil-fuel heat input capacity would have a 289,080 MWh 12 month potential electrical output capacity). For electric utility combined cycle gas turbines the potential electrical output capacity is determined on the basis of the fossil-fuel firing capacity of the steam generator exclusive of the heat input and electrical power contribution by the gas turbine.

Principal company means the electric utility company or companies which own the affected facility.

Resource recovery unit means a facility that combusts more than 75 percent non-fossil fuel on a quarterly (calendar) heat input basis.

Responsible official means responsible official as defined in 40 CFR 70.2.

Solid-derived fuel means any solid, liquid, or gaseous fuel derived from solid fuel for the purpose of creating useful heat and includes, but is not limited to, solvent refined coal, liquified coal, synthetic gas, gasified coal, gasified petroleum coke, gasified biomass, and gasified tire derived fuel.

Spare flue gas desulfurization system module means a separate system of SO_2emission control equipment capable of treating an amount of flue gas equal to the total amount of flue gas generated by an affected facility when operated at maximum capacity divided by the total number of nonspare flue gas desulfurization modules in the system.

Spinning reserve means the sum of the unutilized net generating capability of all units of the electric utility company that are synchronized to the power distribution system and that are capable of immediately accepting additional load. The electric generating capability of equipment under multiple ownership is prorated based on ownership unless the proportional entitlement to electric output is otherwise established by contractual arrangement.

Steam generating unit means any furnace, boiler, or other device used for combusting fuel for the purpose of producing steam (including fossil-fuel-fired steam generators associated with combined cycle gas turbines; nuclear steam generators are not included).

Subbituminous coal means coal that is classified as subbituminous A, B, or C according to the American Society of Testing and Materials in ASTM D388 (incorporated by reference, see §60.17).

System emergency reserves means an amount of electric generating capacity equivalent to the rated capacity of the single largest electric generating unit in the electric utility company (including steam generating units, internal combustion engines, gas turbines, nuclear units, hydroelectric units, and all other electric generating equipment) which is interconnected with the affected facility that has the malfunctioning flue gas desulfurization system. The electric generating capability of equipment under multiple ownership is prorated based on ownership unless the proportional entitlement to electric output is otherwise established by contractual arrangement.

System load means the entire electric demand of an electric utility company's service area interconnected with the affected facility that has the malfunctioning flue gas desulfurization system plus firm contractual sales to other electric utility companies. Sales to other electric utility companies (*e.g.* , emergency power) not on a firm contractual basis may also be included in the system load when no available system capacity exists in the electric utility company to which the power is supplied for sale.

Wet flue gas desulfurization technology or *wet FGD* means a SO_2control system that is located downstream of the steam generating unit and removes sulfur oxides from the combustion gases of the steam generating unit by contacting the combustion gases with an alkaline slurry or solution and forming a liquid material. This definition applies to devices where the aqueous liquid material product of this contact is subsequently converted to other forms. Alkaline reagents used in wet FGD technology include, but are not limited to, lime, limestone, and sodium.

§ 60.42Da Standard for particulate matter (PM).

(a) On and after the date on which the initial performance test is completed or required to be completed under §60.8, whichever date comes first, no owner or operator subject to the provisions of this subpart shall cause to be discharged into the atmosphere from any affected facility for which construction, reconstruction, or modification commenced before or on February 28, 2005, any gases that contain PM in excess of:

(1) 13 ng/J (0.03 lb/MMBtu) heat input derived from the combustion of solid, liquid, or gaseous fuel;

(2) 1 percent of the potential combustion concentration (99 percent reduction) when combusting solid fuel; and

(3) 30 percent of potential combustion concentration (70 percent reduction) when combusting liquid fuel.

(b) On and after the date the initial PM performance test is completed or required to be completed under §60.8, whichever date comes first, no owner or operator subject to the provisions of this subpart shall cause to be discharged into the atmosphere from any affected facility any gases which exhibit greater than 20 percent opacity (6-minute average), except for one 6-minute period per hour of not more than 27 percent opacity.

(c) Except as provided in paragraph (d) of this section, on and after the date on which the initial performance test is completed or required to be completed under §60.8, whichever date comes first, no owner or operator of an affected facility that commenced construction, reconstruction, or modification after February 28, 2005 shall cause to be discharged into the atmosphere from that affected facility any gases that contain PM in excess of either:

(1) 18 ng/J (0.14 lb/MWh) gross energy output; or

(2) 6.4 ng/J (0.015 lb/MMBtu) heat input derived from the combustion of solid, liquid, or gaseous fuel.

(d) As an alternative to meeting the requirements of paragraph (c) of this section, the owner or operator of an affected facility for which construction, reconstruction, or modification commenced after February 28, 2005, may elect to meet the requirements of this paragraph. On and after the date on which the initial performance test is completed or required to be completed under §60.8, whichever date comes first, no owner or operator of an affected facility shall cause to be discharged into the atmosphere from that affected facility for which construction, reconstruction, or modification commenced after February 28, 2005, any gases that contain PM in excess of:

(1) 13 ng/J (0.03 lb/MMBtu) heat input derived from the combustion of solid, liquid, or gaseous fuel, and

(2) 0.1 percent of the combustion concentration determined according to the procedure in §60.48Da(o)(5) (99.9 percent reduction) for an affected facility for which construction or reconstruction commenced after February 28, 2005 when combusting solid, liquid, or gaseous fuel, or

(3) 0.2 percent of the combustion concentration determined according to the procedure in §60.48Da(o)(5) (99.8 percent reduction) for an affected facility for which modification commenced after February 28, 2005 when combusting solid, liquid, or gaseous fuel.

§ 60.43Da Standard for sulfur dioxide (SO2).

(a) On and after the date on which the initial performance test is completed or required to be completed under §60.8, whichever date comes first, no owner or operator subject to the provisions of this subpart shall cause to be discharged into the atmosphere from any affected facility which combusts solid fuel or solid-derived fuel and for which construction, reconstruction, or modification commenced before or on February 28, 2005, except as provided under paragraphs (c), (d), (f) or (h) of this section, any gases that contain SO_2 in excess of:

(1) 520 ng/J (1.20 lb/MMBtu) heat input and 10 percent of the potential combustion concentration (90 percent reduction); or

(2) 30 percent of the potential combustion concentration (70 percent reduction), when emissions are less than 260 ng/J (0.60 lb/MMBtu) heat input.

(b) On and after the date on which the initial performance test is completed or required to be completed under §60.8, whichever date comes first, no owner or operator subject to the provisions of this subpart shall cause to be discharged into the atmosphere from any affected facility which combusts liquid or gaseous fuels (except for liquid or gaseous fuels derived from solid fuels and as provided under paragraphs (e) or (h) of this section) and for which construction, reconstruction, or modification commenced before or on February 28, 2005, any gases that contain SO_2 in excess of:

(1) 340 ng/J (0.80 lb/MMBtu) heat input and 10 percent of the potential combustion concentration (90 percent reduction); or

(2) 100 percent of the potential combustion concentration (zero percent reduction) when emissions are less than 86 ng/J (0.20 lb/MMBtu) heat input.

(c) On and after the date on which the initial performance test is completed or required to be completed under §60.8, whichever date comes first, no owner or operator subject to the provisions of this subpart shall cause to be discharged into the atmosphere from any affected facility which combusts solid solvent refined coal (SRC–I) any gases that contain SO_2 in excess of 520 ng/J (1.20 lb/MMBtu) heat input and 15 percent of the potential combustion concentration (85 percent reduction) except as provided under paragraph (f) of this section; compliance with the emission limitation is determined on a 30-day rolling average basis and compliance with the percent reduction requirement is determined on a 24-hour basis.

(d) Sulfur dioxide emissions are limited to 520 ng/J (1.20 lb/MMBtu) heat input from any affected facility which:

(1) Combusts 100 percent anthracite;

(2) Is classified as a resource recovery unit; or

(3) Is located in a noncontinental area and combusts solid fuel or solid-derived fuel.

(e) Sulfur dioxide emissions are limited to 340 ng/J (0.80 lb/MMBtu) heat input from any affected facility which is located in a noncontinental area and combusts liquid or gaseous fuels (excluding solid-derived fuels).

(f) The emission reduction requirements under this section do not apply to any affected facility that is operated under an SO_2 commercial demonstration permit issued by the Administrator in accordance with the provisions of §60.47Da.

(g) Compliance with the emission limitation and percent reduction requirements under this section are both determined on a 30-day rolling average basis except as provided under paragraph (c) of this section.

(h) When different fuels are combusted simultaneously, the applicable standard is determined by proration using the following formula:

(1) If emissions of SO_2 to the atmosphere are greater than 260 ng/J (0.60 lb/MMBtu) heat input

$$E_s = \frac{(340x + 520y)}{100} \quad \text{and} \quad \%P_s = 10$$

(2) If emissions of SO_2 to the atmosphere are equal to or less than 260 ng/J (0.60 lb/MMBtu) heat input:

$$E_s = \frac{(340x + 520y)}{100} \quad \text{and} \quad \%P_s = \frac{(10x + 30y)}{100}$$

Where:

E_s= Prorated SO$_2$emission limit (ng/J heat input);

$\%P_s$= Percentage of potential SO$_2$emission allowed;

x = Percentage of total heat input derived from the combustion of liquid or gaseous fuels (excluding solid-derived fuels); and

y = Percentage of total heat input derived from the combustion of solid fuel (including solid-derived fuels).

(i) Except as provided in paragraphs (j) and (k) of this section, on and after the date on which the initial performance test is completed or required to be completed under §60.8, whichever date comes first, no owner or operator of an affected facility that commenced construction, reconstruction, or modification commenced after February 28, 2005 shall cause to be discharged into the atmosphere from that affected facility, any gases that contain SO$_2$in excess of the applicable emission limitation specified in paragraphs (i)(1) through (3) of this section.

(1) For an affected facility for which construction commenced after February 28, 2005, any gases that contain SO$_2$in excess of either:

(i) 180 ng/J (1.4 lb/MWh) gross energy output on a 30-day rolling average basis; or

(ii) 5 percent of the potential combustion concentration (95 percent reduction) on a 30-day rolling average basis.

(2) For an affected facility for which reconstruction commenced after February 28, 2005, any gases that contain SO$_2$in excess of either:

(i) 180 ng/J (1.4 lb/MWh) gross energy output on a 30-day rolling average basis;

(ii) 65 ng/J (0.15 lb/MMBtu) heat input on a 30-day rolling average basis; or

(iii) 5 percent of the potential combustion concentration (95 percent reduction) on a 30-day rolling average basis.

(3) For an affected facility for which modification commenced after February 28, 2005, any gases that contain SO$_2$in excess of either:

(i) 180 ng/J (1.4 lb/MWh) gross energy output on a 30-day rolling average basis;

(ii) 65 ng/J (0.15 lb/MMBtu) heat input on a 30-day rolling average basis; or

(iii) 10 percent of the potential combustion concentration (90 percent reduction) on a 30-day rolling average basis.

(j) On and after the date on which the initial performance test is completed or required to be completed under §60.8, whichever date comes first, no owner or operator of an affected facility that commenced construction, reconstruction, or modification commenced after February 28, 2005, and that burns 75 percent or more (by heat input) coal refuse on a 12-month rolling average basis, shall caused to be discharged into the atmosphere from that affected facility any gases that contain SO$_2$in excess of the applicable emission limitation specified in paragraphs (j)(1) through (3) of this section.

(1) For an affected facility for which construction commenced after February 28, 2005, any gases that contain SO$_2$in excess of either:

(i) 180 ng/J (1.4 lb/MWh) gross energy output on a 30-day rolling average basis; or

(ii) 6 percent of the potential combustion concentration (94 percent reduction) on a 30-day rolling average basis.

(2) For an affected facility for which reconstruction commenced after February 28, 2005, any gases that contain SO$_2$in excess of either:

(i) 180 ng/J (1.4 lb/MWh) gross energy output on a 30-day rolling average basis;

(ii) 65 ng/J (0.15 lb/MMBtu) heat input on a 30-day rolling average basis; or

(iii) 6 percent of the potential combustion concentration (94 percent reduction) on a 30-day rolling average basis.

(3) For an affected facility for which modification commenced after February 28, 2005, any gases that contain SO$_2$in excess of either:

(i) 180 ng/J (1.4 lb/MWh) gross energy output on a 30-day rolling average basis;

(ii) 65 ng/J (0.15 lb/MMBtu) heat input on a 30-day rolling average basis; or

(iii) 10 percent of the potential combustion concentration (90 percent reduction) on a 30-day rolling average basis.

(k) On and after the date on which the initial performance test is completed or required to be completed under §60.8, whichever date comes first, no owner or operator of an affected facility located in a noncontinental area that commenced construction, reconstruction, or modification commenced after February 28, 2005, shall cause to be discharged into the atmosphere from that affected facility any gases that contain SO$_2$in excess of the applicable emission limitation specified in paragraphs (k)(1) and (2) of this section.

(1) For an affected facility that burns solid or solid-derived fuel, the owner or operator shall not cause to be discharged into the atmosphere any gases that contain SO$_2$in excess of 520 ng/J (1.2 lb/MMBtu) heat input on a 30-day rolling average basis.

(2) For an affected facility that burns other than solid or solid-derived fuel, the owner or operator shall not cause to be discharged into the atmosphere any gases that contain SO$_2$in excess of if the affected facility or 230 ng/J (0.54 lb/MMBtu) heat input on a 30-day rolling average basis.

§ 60.44Da Standard for nitrogen oxides (NOX).

(a) On and after the date on which the initial performance test is completed or required to be completed under §60.8, whichever date comes first, no owner or operator subject to the provisions of this subpart shall cause to be discharged into the atmosphere from any affected facility, except as provided under paragraphs (b), (d), (e), and (f) of this section, any gases that contain NO$_X$(expressed as NO$_2$) in excess of the following emission limits, based on a 30-day rolling average basis, except as provided under §60.48Da(j)(1):

(1) NO$_X$emission limits.

Fuel type	Emission limit for heat input	
	ng/J	lb/MMBtu
Gaseous fuels:		
Coal-derived fuels	210	0.50
All other fuels	86	0.20
Liquid fuels:		
Coal-derived fuels	210	0.50
Shale oil	210	0.50
All other fuels	130	0.30
Solid fuels:		
Coal-derived fuels	210	0.50
Any fuel containing more than 25%, by weight, coal refuse	(1)	(1)
Any fuel containing more than 25%, by weight, lignite if the lignite is mined in North Dakota, South Dakota, or Montana, and is combusted in a slag tap furnace[2]	340	0.80
Any fuel containing more than 25%, by weight, lignite not subject to the 340 ng/J heat input emission limit[2]	260	0.60
Subbituminous coal	210	0.50
Bituminous coal	260	0.60
Anthracite coal	260	0.60
All other fuels	260	0.60

[1] Exempt from NO_xstandards and NO_xmonitoring requirements.

[2] Any fuel containing less than 25%, by weight, lignite is not prorated but its percentage is added to the percentage of the predominant fuel.

(2) NO_xreduction requirement.

Fuel type	Percent reduction of potential combustion concentration
Gaseous fuels	25
Liquid fuels	30
Solid fuels	65

(b) The emission limitations under paragraph (a) of this section do not apply to any affected facility which is combusting coal-derived liquid fuel and is operating under a commercial demonstration permit issued by the Administrator in accordance with the provisions of §60.47Da.

(c) Except as provided under paragraphs (d), (e), and (f) of this section, when two or more fuels are combusted simultaneously, the applicable standard is determined by proration using the following formula:

$$E_n = \frac{(86w + 130x + 210y + 260z + 340v)}{100}$$

Where:

E_n= Applicable standard for $NO_x$when multiple fuels are combusted simultaneously (ng/J heat input);

w = Percentage of total heat input derived from the combustion of fuels subject to the 86 ng/J heat input standard;

x = Percentage of total heat input derived from the combustion of fuels subject to the 130 ng/J heat input standard;

y = Percentage of total heat input derived from the combustion of fuels subject to the 210 ng/J heat input standard;

z = Percentage of total heat input derived from the combustion of fuels subject to the 260 ng/J heat input standard; and

v = Percentage of total heat input delivered from the combustion of fuels subject to the 340 ng/J heat input standard.

(d)(1) On and after the date on which the initial performance test is completed or required to be completed under §60.8, whichever date comes first, no owner or operator of an affected facility that commenced construction after July 9, 1997, but before or on February 28, 2005 shall cause to be discharged into the atmosphere any gases that contain NO_x(expressed as NO_2) in excess of 200 ng/J (1.6 lb/MWh) gross energy output, based on a 30-day rolling average basis, except as provided under §60.48Da(k).

(2) On and after the date on which the initial performance test is completed or required to be completed under §60.8, whichever date comes first, no owner or operator of affected facility for which reconstruction commenced after July 9, 1997, but before or on February 28, 2005 shall cause to be discharged into the atmosphere any gases that contain NO_x(expressed as NO_2) in excess of 65 ng/J (0.15 lb/MMBtu) heat input, based on a 30-day rolling average basis.

(e) Except for an IGCC electric utility steam generating unit meeting the requirements of paragraph (f) of this section, on and after the date on which the initial performance test is completed or required to be completed under §60.8, whichever date comes first, no owner or operator of an affected facility that commenced construction, reconstruction, or modification after February 28, 2005 shall cause to be discharged into the atmosphere from that affected facility any gases that contain NO_x(expressed as NO_2) in excess of the applicable emission limitation specified in paragraphs (e)(1) through (3) of this section.

(1) For an affected facility for which construction commenced after February 28, 2005, the owner or operator shall not cause to be discharged into the atmosphere any gases that contain NO_x(expressed as NO_2) in excess of 130 ng/J (1.0 lb/MWh) gross energy output on a 30-day rolling average basis, except as provided under §60.48Da(k).

(2) For an affected facility for which reconstruction commenced after February 28, 2005, the owner or operator shall not cause to be

discharged into the atmosphere any gases that contain NO_X(expressed as NO_2) in excess of either:

(i) 130 ng/J (1.0 lb/MWh) gross energy output on a 30-day rolling average basis; or

(ii) 47 ng/J (0.11 lb/MMBtu) heat input on a 30-day rolling average basis.

(3) For an affected facility for which modification commenced after February 28, 2005, the owner or operator shall not cause to be discharged into the atmosphere any gases that contain NO_X(expressed as NO_2) in excess of either:

(i) 180 ng/J (1.4 lb/MWh) gross energy output on a 30-day rolling average basis; or

(ii) 65 ng/J (0.15 lb/MMBtu) heat input on a 30-day rolling average basis.

(f) On and after the date on which the initial performance test is completed or required to be completed under §60.8, whichever date comes first, the owner or operator of an IGCC electric utility steam generating unit subject to the provisions of this subpart and for which construction, reconstruction, or modification commenced after February 28, 2005, shall meet the requirements specified in paragraphs (f)(1) through (3) of this section.

(1) Except as provided for in paragraphs (f)(2) and (3) of this section, the owner or operator shall not cause to be discharged into the atmosphere any gases that contain NO_X(expressed as NO_2) in excess of 130 ng/J (1.0 lb/MWh) gross energy output on a 30-day rolling average basis.

(2) When burning liquid fuel exclusively or in combination with solid-derived fuel such that the liquid fuel contributes 50 percent or more of the total heat input to the combined cycle combustion turbine, the owner or operator shall not cause to be discharged into the atmosphere any gases that contain NO_X(expressed as NO_2) in excess of 190 ng/J (1.5 lb/MWh) gross energy output on a 30-day rolling average basis.

(3) In cases when during a 30-day rolling average compliance period liquid fuel is burned in such a manner to meet the conditions in paragraph (f)(2) of this section for only a portion of the clock hours in the 30-day period, the owner or operator shall not cause to be discharged into the atmosphere any gases that contain NO_X(expressed as NO_2) in excess of the computed weighted-average emissions limit based on the proportion of gross energy output (in MWh) generated during the compliance period for each of emissions limits in paragraphs (f)(1) and (2) of this section.

§ 60.45Da Standard for mercury (Hg).

(a) For each coal-fired electric utility steam generating unit other than an IGCC electric utility steam generating unit, on and after the date on which the initial performance test is completed or required to be completed under §60.8, whichever date comes first, no owner or operator subject to the provisions of this subpart shall cause to be discharged into the atmosphere from any affected facility for which construction, modification, or reconstruction commenced after January 30, 2004, any gases that contain mercury (Hg) emissions in excess of each Hg emissions limit in paragraphs (a)(1) through (5) of this section that applies to you. The Hg emissions limits in paragraphs (a)(1) through (5) of this section are based on a 12-month rolling average basis using the procedures in §60.50Da(h).

(1) For each coal-fired electric utility steam generating unit that burns only bituminous coal, you must not discharge into the atmosphere any gases from a new affected source that contain Hg in excess of 20×10^{-6} pound per megawatt hour (lb/MWh) or 0.020 lb/gigawatt-hour (GWh) on an output basis. The International System of Units (SI) equivalent is 0.0025 ng/J.

(2) For each coal-fired electric utility steam generating unit that burns only subbituminous coal:

(i) If your unit is located in a county-level geographical area receiving greater than 25 inches per year (in/yr) mean annual precipitation, based on the most recent publicly available U.S. Department of Agriculture 30-year data, you must not discharge into the atmosphere any gases from a new affected source that contain Hg in excess of 66×10^{-6} lb/MWh or 0.066 lb/GWh on an output basis. The SI equivalent is 0.0083 ng/J.

(ii) If your unit is located in a county-level geographical area receiving less than or equal to 25 in/yr mean annual precipitation, based on the most recent publicly available U.S. Department of Agriculture 30-year data, you must not discharge into the atmosphere any gases from a new affected source that contain Hg in excess of 97×10^{-6} lb/MWh or 0.097 lb/GWh on an output basis. The SI equivalent is 0.0122 ng/J.

(3) For each coal-fired electric utility steam generating unit that burns only lignite, you must not discharge into the atmosphere any gases from a new affected source that contain Hg in excess of 175×10^{-6} lb/MWh or 0.175 lb/GWh on an output basis. The SI equivalent is 0.0221 ng/J.

(4) For each coal-burning electric utility steam generating unit that burns only coal refuse, you must not discharge into the atmosphere any gases from a new affected source that contain Hg in excess of 16×10^{-6} lb/MWh or 0.016 lb/GWh on an output basis. The SI equivalent is 0.0020 ng/J.

(5) For each coal-fired electric utility steam generating unit that burns a blend of coals from different coal ranks (*i.e.* , bituminous coal, subbituminous coal, lignite) or a blend of coal and coal refuse, you must not discharge into the atmosphere any gases from a new affected source that contain Hg in excess of the unit-specific Hg emissions limit established according to paragraph (a)(5)(i) or (ii) of this section, as applicable to the affected unit.

(i) If you operate a coal-fired electric utility steam generating unit that burns a blend of coals from different coal ranks or a blend of coal and coal refuse, you must not discharge into the atmosphere any gases from a new affected source that contain Hg in excess of the computed weighted Hg emissions limit based on the Btu, MWh, or MJ) contributed by each coal rank burned during the compliance period and its applicable Hg emissions limit in paragraphs (a)(1) through (4) of this section as determined using Equation 1 in this section. For each affected source, you must comply with the weighted Hg emissions limit calculated using Equation 1 in this section based on the total Hg emissions from the unit and the total Btu, MWh, or MJ contributed by all fuels burned during the compliance period.

$$EL_b = \frac{\sum_{i=1}^{n} EL_i(HH_i)}{\sum_{i=1}^{n} HH_i} \qquad \text{(Eq. 1)}$$

Where:

EL_b= Total allowable Hg in lb/MWh that can be emitted to the atmosphere from any affected source being averaged according to this paragraph.

EL_i= Hg emissions limit for the subcategory i (coal rank) that applies to affected source, lb/MWh;

HH_i= For each affected source, the Btu, MWh, or MJ contributed by the corresponding subcategory i (coal rank) burned during the compliance period; and

n = Number of subcategories (coal ranks) being averaged for an affected source.

(ii) If you operate a coal-fired electric utility steam generating unit that burns a blend of coals from different coal ranks or a blend of coal and coal refuse together with one or more non-regulated, supplementary fuels, you must not discharge into the atmosphere any gases from a new affected source that contain Hg in excess of the computed weighted Hg emission limit based on the Btu, MWh, or MJ contributed by each coal rank burned during the compliance period and its applicable Hg emissions limit in paragraphs (a)(1) through (4) of this section as determined using Equation 1 in this section. For each affected source. You must comply with the weighted Hg emissions limit calculated using Equation 1 in this section based on the total Hg emissions from the unit contributed by both regulated and nonregulated fuels burned during the compliance period and the total Btu, MWh, or MJ contributed by both regulated and nonregulated fuels burned during the compliance period.

(b) For each IGCC electric utility steam generating unit, on and after the date on which the initial performance test required to be conducted under §60.8 is completed, no owner or operator subject to the provisions of this subpart shall cause to be discharged into the atmosphere from any affected facility for which construction, modification, or reconstruction commenced after January 30, 2004, any gases that contain Hg emissions in excess of 20×10^{-6} lb/MWh or 0.020 lb/GWh on an output basis. The SI equivalent is 0.0025 ng/J. This Hg emissions limit is based on a 12-month rolling average basis using the procedures in §60.50Da(h).

§ 60.46Da [Reserved]

§ 60.47Da Commercial demonstration permit.

(a) An owner or operator of an affected facility proposing to demonstrate an emerging technology may apply to the Administrator for a commercial demonstration permit. The Administrator will issue a commercial demonstration permit in accordance with paragraph (e) of this section. Commercial demonstration permits may be issued only by the Administrator, and this authority will not be delegated.

(b) An owner or operator of an affected facility that combusts solid solvent refined coal (SRC–I) and who is issued a commercial demonstration permit by the Administrator is not subject to the SO_2emission reduction requirements under §60.43Da(c) but must, as a minimum, reduce SO_2emissions to 20 percent of the potential combustion concentration (80 percent reduction) for each 24-hour period of steam generator operation and to less than 520 ng/J (1.20 lb/MMBtu) heat input on a 30-day rolling average basis.

(c) An owner or operator of a fluidized bed combustion electric utility steam generator (atmospheric or pressurized) who is issued a commercial demonstration permit by the Administrator is not subject to the SO_2emission reduction requirements under §60.43Da(a) but must, as a minimum, reduce SO_2emissions to 15 percent of the potential combustion concentration (85 percent reduction) on a 30-day rolling average basis and to less than 520 ng/J (1.20 lb/MMBtu) heat input on a 30-day rolling average basis.

(d) The owner or operator of an affected facility that combusts coal-derived liquid fuel and who is issued a commercial demonstration permit by the Administrator is not subject to the applicable NO_Xemission limitation and percent reduction under §60.44Da(a) but must, as a minimum, reduce emissions to less than 300 ng/J (0.70 lb/MMBtu) heat input on a 30-day rolling average basis.

(e) Commercial demonstration permits may not exceed the following equivalent MW electrical generation capacity for any one technology category, and the total equivalent MW electrical generation capacity for all commercial demonstration plants may not exceed 15,000 MW.

Technology	Pollutant	Equivalent electrical capacity (MW electrical output)
Solid solvent refined coal (SCR I)	SO2	6,000–10,000
Fluidized bed combustion (atmospheric)	SO2	400–3,000
Fluidized bed combustion (pressurized)	SO2	400–1,200
Coal liquification	NOX	750–10,000
Total allowable for all technologies		15,000

§ 60.48Da Compliance provisions.

(a) Compliance with the PM emission limitation under §60.42Da(a)(1) constitutes compliance with the percent reduction requirements for PM under §60.42Da(a)(2) and (3).

(b) Compliance with the NO_Xemission limitation under §60.44Da(a)(1) constitutes compliance with the percent reduction requirements under §60.44Da(a)(2).

(c) The PM emission standards under §60.42Da, the NO_Xemission standards under §60.44Da, and the Hg emission standards under §60.45Da apply at all times except during periods of startup, shutdown, or malfunction.

(d) During emergency conditions in the principal company, an affected facility with a malfunctioning flue gas desulfurization system may be operated if SO_2emissions are minimized by:

(1) Operating all operable flue gas desulfurization system modules, and bringing back into operation any malfunctioned module as soon as repairs are completed,

(2) Bypassing flue gases around only those flue gas desulfurization system modules that have been taken out of operation because they were incapable of any SO_2emission reduction or which would have suffered significant physical damage if they had remained in operation, and

(3) Designing, constructing, and operating a spare flue gas desulfurization system module for an affected facility larger than 365 MW (1,250 MMBtu/hr) heat input (approximately 125 MW electrical output capacity). The Administrator may at his discretion require the owner or operator within 60 days of notification to demonstrate spare module capability. To demonstrate this capability, the owner or operator must demonstrate compliance with the appropriate requirements under paragraph under §60.43Da(a), (b), (d), (e), and (h) for any period of operation lasting from 24 hours to 30 days when:

(i) Any one flue gas desulfurization module is not operated.

(ii) The affected facility is operating at the maximum heat input rate,

(iii) The fuel fired during the 24-hour to 30-day period is representative of the type and average sulfur content of fuel used over a typical 30-day period, and

(iv) The owner or operator has given the Administrator at least 30 days notice of the date and period of time over which the *demonstration will be performed.*

(e) After the initial performance test required under §60.8, compliance with the SO_2emission limitations and percentage reduction requirements under §60.43Da and the NO_Xemission limitations under §60.44Da is based on the average emission rate for 30 successive boiler operating days. A separate performance test is completed at the end of each boiler operating day after the initial performance test, and a new 30 day average emission rate for both $SO_2$and $NO_X$and a new percent reduction for $SO_2$are calculated to show compliance with the standards.

(f) For the initial performance test required under §60.8, compliance with the SO_2emission limitations and percent reduction requirements under §60.43Da and the NO_Xemission limitation under §60.44Da is based on the average emission rates for SO_2, NO_X, and percent reduction for $SO_2$for the first 30 successive boiler operating days. The initial performance test is the only test in which at least 30 days prior notice is required unless otherwise specified by the Administrator. The initial performance test is to be scheduled so that the first boiler operating day of the 30 successive boiler operating days is completed within 60 days after achieving the maximum production rate at which the affected facility will be operated, but not later than 180 days after initial startup of the facility.

(g) The owner or operator of an affected facility subject to emission limitations in this subpart shall determine compliance as follows:

(1) Compliance with applicable 30-day rolling average $SO_2$and NO_Xemission limitations is determined by calculating the arithmetic average of all hourly emission rates for $SO_2$and $NO_X$for the 30 successive boiler operating days, except for data obtained during startup, shutdown, malfunction (NO_Xonly), or emergency conditions (SO_2only).

(2) Compliance with applicable SO_2percentage reduction requirements is determined based on the average inlet and outlet SO_2emission rates for the 30 successive boiler operating days.

(3) Compliance with applicable daily average PM emission limitations is determined by calculating the arithmetic average of all hourly emission rates for PM each boiler operating day, except for data obtained during startup, shutdown, and malfunction. Averages are only calculated for boiler operating days that have valid data for at least 18 hours of unit operation during which the standard applies. Instead, the valid hourly emission rates are averaged with the next boiler operating day with 18 hours or more of valid PM CEMS data to determine compliance.

(h) If an owner or operator has not obtained the minimum quantity of emission data as required under §60.49Da of this subpart, compliance of the affected facility with the emission requirements under §§60.43Da and 60.44Da of this subpart for the day on which the 30-day period ends may be determined by the Administrator by following the applicable procedures in section 7 of Method 19 of appendix A of this part.

(i) *Compliance provisions for sources subject to §60.44Da(d)(1), (e)(1), (e)(2)(i), (e)(3)(i), or (f)* . The owner or operator of an affected facility subject to §60.44Da(d)(1), (e)(1), (e)(2)(i), (e)(3)(i), or (f) shall calculate NO_Xemissions as 1.194×10^{-7} lb/scf-ppm times the average hourly NO_Xoutput concentration in ppm (measured according to the provisions of §60.49Da(c)), times the average hourly flow rate (measured in scfh, according to the provisions of §60.49Da(l) or §60.49Da(m)), divided by the average hourly gross energy output (measured according to the provisions of §60.49Da(k)). Alternatively, for oil-fired and gas-fired units, NO_Xemissions may be calculated by multiplying the hourly NO_Xemission rate in lb/MMBtu (measured by the CEMS required under §§60.49Da(c) and (d)), by the hourly heat input rate (measured according to the provisions of §60.49Da(n)), and dividing the result by the average gross energy output (measured according to the provisions of §60.49Da(k)).

(j) *Compliance provisions for duct burners subject to §60.44Da(a)(1)* . To determine compliance with the emissions limits for NO_Xrequired by *§60.44Da(a) for duct burners used in combined cycle systems, either* of the procedures described in paragraph (j)(1) or (2) of this section *may be used:*

(1) The owner or operator of an affected duct burner shall conduct the performance test required under §60.8 using the appropriate methods in appendix A of this part. Compliance with the emissions limits under §60.44Da(a)(1) is determined on the average of three (nominal 1-hour) runs for the initial and subsequent performance tests. During the performance test, one sampling site shall be located in the exhaust of the turbine prior to the duct burner. A second sampling site shall be located at the outlet from the heat recovery steam generating unit. Measurements shall be taken at both sampling sites during the performance test; or

(2) The owner or operator of an affected duct burner may elect to determine compliance by using the continuous emission monitoring system (CEMS) specified under §60.49Da for measuring $NO_X$and oxygen (O_2) (or carbon dioxide (CO_2)) and meet the requirements of §60.49Da. Alternatively, data from a NO_Xemission rate (*i.e.* , NO_X-diluent) CEMS certified according to the provisions of §75.20(c) of this chapter and appendix A to part 75 of this chapter, and meeting the quality assurance requirements of §75.21 of this chapter and appendix B to part 75 of this chapter, may be used, with the following caveats. Data used to meet the requirements of §60.51Da shall not include substitute data values derived from the missing data procedures in subpart D of part 75 of this chapter, nor shall the data have been bias adjusted according to the procedures of part 75 of this chapter. The sampling site shall be located at the outlet from the steam generating unit. The NO_Xemission rate at the outlet from the steam generating unit shall constitute the NO_Xemission rate from the duct burner of the combined cycle system.

(k) *Compliance provisions for duct burners subject to §60.44Da(d)(1) or (e)(1)* . To determine compliance with the emission limitation for NO_Xrequired by §60.44Da(d)(1) or (e)(1) for duct burners used in combined cycle systems, either of the procedures described in paragraphs (k)(1) and (2) of this section may be used:

(1) The owner or operator of an affected duct burner used in combined cycle systems shall determine compliance with the applicable NO_Xemission limitation in §60.44Da(d)(1) or (e)(1) as follows:

(i) The emission rate (E) of NO_Xshall be computed using Equation 2 in this section:

$$E = \frac{(C_{sg} \times Q_{sg}) - (C_{te} \times Q_{te})}{(O_{sg} \times h)} \qquad \text{(Eq. 2)}$$

Where:

E = Emission rate of $NO_X$from the duct burner, ng/J (lb/MWh) gross output;

C_{sg}= Average hourly concentration of NO$_X$ exiting the steam generating unit, ng/dscm (lb/dscf);

C_{te}= Average hourly concentration of NO$_X$ in the turbine exhaust upstream from duct burner, ng/dscm (lb/dscf);

Q_{sg}= Average hourly volumetric flow rate of exhaust gas from steam generating unit, dscm/hr (dscf/hr);

Q_{te}= Average hourly volumetric flow rate of exhaust gas from combustion turbine, dscm/hr (dscf/hr);

O_{sg}= Average hourly gross energy output from steam generating unit, J (MWh); and

h = Average hourly fraction of the total heat input to the steam generating unit derived from the combustion of fuel in the affected duct burner.

(ii) Method 7E of appendix A of this part shall be used to determine the NO$_X$ concentrations (C_{sg} and C_{te}). Method 2, 2F or 2G of appendix A of this part, as appropriate, shall be used to determine the volumetric flow rates (Q_{sg} and Q_{te}) of the exhaust gases. The volumetric flow rate measurements shall be taken at the same time as the concentration measurements.

(iii) The owner or operator shall develop, demonstrate, and provide information satisfactory to the Administrator to determine the average hourly gross energy output from the steam generating unit, and the average hourly percentage of the total heat input to the steam generating unit derived from the combustion of fuel in the affected duct burner.

(iv) Compliance with the applicable NO$_X$ emission limitation in §60.44Da(d)(1) or (e)(1) is determined by the three-run average (nominal 1-hour runs) for the initial and subsequent performance tests.

(2) The owner or operator of an affected duct burner used in a combined cycle system may elect to determine compliance with the applicable NO$_X$ emission limitation in §60.44Da(d)(1) or (e)(1) on a 30-day rolling average basis as indicated in paragraphs (k)(2)(i) through (iv) of this section.

(i) The emission rate (E) of NO$_X$ shall be computed using Equation 3 in this section:

$$E = \frac{(C_{sg} \times Q_{sg})}{O_{cc}} \qquad \text{(Eq. 3)}$$

Where:

E = Emission rate of NO$_X$ from the duct burner, ng/J (lb/MWh) gross output;

C_{sg}= Average hourly concentration of NO$_X$ exiting the steam generating unit, ng/dscm (lb/dscf);

Q_{sg}= Average hourly volumetric flow rate of exhaust gas from steam generating unit, dscm/hr (dscf/hr); and

O_{cc}= Average hourly gross energy output from entire combined cycle unit, J (MWh).

(ii) The CEMS specified under §60.49Da for measuring NO$_X$ and O_2 (or CO_2) shall be used to determine the average hourly NO$_X$ concentrations (C_{sg}). The continuous flow monitoring system specified in §60.49Da(l) or §60.49Da(m) shall be used to determine the volumetric flow rate (Q_{sg}) of the exhaust gas. If the option to use the flow monitoring system in §60.49Da(m) is selected, the flow rate data used to meet the requirements of §60.51Da shall not include substitute data values derived from the missing data procedures in subpart D of part 75 of this chapter, nor shall the data have been bias adjusted according to the procedures of part 75 of this chapter. The sampling site shall be located at the outlet from the steam generating unit.

(iii) The continuous monitoring system specified under §60.49Da(k) for measuring and determining gross energy output shall be used to determine the average hourly gross energy output from the entire combined cycle unit (O_{cc}), which is the combined output from the combustion turbine and the steam generating unit.

(iv) The owner or operator may, in lieu of installing, operating, and recording data from the continuous flow monitoring system specified in §60.49Da(l), determine the mass rate (lb/hr) of NO$_X$ emissions by installing, operating, and maintaining continuous fuel flowmeters following the appropriate measurements procedures specified in appendix D of part 75 of this chapter. If this compliance option is selected, the emission rate (E) of NO$_X$ shall be computed using Equation 4 in this section:

$$E = \frac{(ER_{sg} \times H_{cc})}{O_{cc}} \qquad \text{(Eq. 4)}$$

Where:

E = Emission rate of NO$_X$ from the duct burner, ng/J (lb/MWh) gross output;

ER_{sg}= Average hourly emission rate of NO$_X$ exiting the steam generating unit heat input calculated using appropriate F factor as described in Method 19 of appendix A of this part, ng/J (lb/MMBtu);

H_{cc}= Average hourly heat input rate of entire combined cycle unit, J/hr (MMBtu/hr); and

O_{cc}= Average hourly gross energy output from entire combined cycle unit, J (MWh).

(3) When an affected duct burner steam generating unit utilizes a common steam turbine with one or more affected duct burner steam generating units, the owner or operator shall either:

(i) Determine compliance with the applicable NO$_X$ emissions limits by measuring the emissions combined with the emissions from the other unit(s) utilizing the common steam turbine; or

(ii) Develop, demonstrate, and provide information satisfactory to the Administrator on methods for apportioning the combined gross energy output from the steam turbine for each of the affected duct burners. The Administrator may approve such demonstrated substitute methods for apportioning the combined gross energy output measured at the steam turbine whenever the demonstration ensures accurate estimation of emissions regulated under this part.

(l) *Compliance provisions for sources subject to §60.45Da.* The owner or operator of an affected facility subject to §60.45Da (new sources constructed or reconstructed after January 30, 2004) shall calculate the Hg emission rate (lb/MWh) for each calendar month of the year, using hourly Hg concentrations measured according to the provisions of §60.49Da(p) in conjunction with hourly stack gas volumetric flow rates measured according to the provisions of §60.49Da(l) or (m), and hourly gross electrical outputs, determined according to the provisions in §60.49Da(k). Compliance with the applicable standard under §60.45Da is determined on a 12-month rolling average basis.

(m) *Compliance provisions for sources subject to §60.43Da(i)(1)(i), (i)(2)(i), (i)(3)(i), (j)(1)(i), (j)(2)(i), or (j)(3)(i).* The owner or operator of an affected facility subject to §60.43Da(i)(1)(i), (i)(2)(i), (i)(3)(i), (j)(1)(i), (j)(2)(i), or (j)(3)(i) shall calculate SO_2emissions as 1.660×10^{-7}lb/scf-ppm times the average hourly SO_2output concentration in ppm (measured according to the provisions of §60.49Da(b)), times the average hourly flow rate (measured according to the provisions of §60.49Da(l) or §60.49Da(m)), divided by the average hourly gross energy output (measured according to the provisions of §60.49Da(k)). Alternatively, for oil-fired and gas-fired units, SO_2emissions may be calculated by multiplying the hourly SO_2emission rate (in lb/MMBtu), measured by the CEMS required under §60.49Da, by the hourly heat input rate (measured according to the provisions of §60.49Da(n)), and dividing the result by the average gross energy output (measured according to the provisions of §60.49Da(k)).

(n) *Compliance provisions for sources subject to §60.42Da(c)(1).* The owner or operator of an affected facility subject to §60.42Da(c)(1) shall calculate PM emissions by multiplying the average hourly PM output concentration, measured according to the provisions of §60.49Da(t), by the average hourly flow rate, measured according to the provisions of §60.49Da(l), and divided by the average hourly gross energy output, measured according to the provisions of §60.49Da(k). Compliance with the emission limit is determined by calculating the arithmetic average of the hourly emission rates computed for each boiler operating day.

(o) *Compliance provisions for sources subject to §60.42Da(c)(2) or (d).* Except as provided for in paragraph (p) of this section, the owner or operator of an affected facility for which construction, reconstruction, or modification commenced after February 28, 2005, shall demonstrate compliance with each applicable emission limit according to the requirements in paragraphs (o)(1) through (o)(5) of this section and use a COMS to demonstrate compliance with §60.42Da(b).

(1) You must conduct a performance test to demonstrate initial compliance with the applicable PM emissions limit in 60.42Da(c)(2) or (d) by the applicable date specified in §60.8(a). Thereafter, you must conduct each subsequent performance test within 12 calendar months of the date of the prior performance test. You must conduct each performance test according to the requirements in §60.8 using the test methods and procedures in §60.50Da.

(2) You must monitor the performance of each electrostatic precipitator or fabric filter (baghouse) operated to comply with the applicable PM emissions limit in §60.42Da(c)(2) or (d) using a continuous opacity monitoring system (COMS) according to the requirements in paragraphs (o)(2)(i) through (vi) unless you elect to comply with one of the alternatives provided in paragraphs (o)(3) and (o)(4) of this section, as applicable to your control device.

(i) Each COMS must meet Performance Specification 1 in 40 CFR part 60, appendix B.

(ii) You must comply with the quality assurance requirements in paragraphs (o)(4)(ii)(A) through (E) of this section.

(A) You must automatically (intrinsic to the opacity monitor) check the zero and upscale (span) calibration drifts at least once daily. For a particular COMS, the acceptable range of zero and upscale calibration materials is as defined in the applicable version of Performance Specification 1 in 40 CFR part 60, appendix B.

(B) You must adjust the zero and span whenever the 24-hour zero drift or 24-hour span drift exceeds 4 percent opacity. The COMS must allow for the amount of excess zero and span drift measured at the 24-hour interval checks to be recorded and quantified. The optical surfaces exposed to the effluent gases must be cleaned prior to performing the zero and span drift adjustments, except for systems using automatic zero adjustments. For systems using automatic zero adjustments, the optical surfaces must be cleaned when the cumulative automatic zero compensation exceeds 4 percent opacity.

(C) You must apply a method for producing a simulated zero opacity condition and an upscale (span) opacity condition using a certified neutral density filter or other related technique to produce a known obscuration of the light beam. All procedures applied must provide a system check of the analyzer internal optical surfaces and all electronic circuitry including the lamp and photodetector assembly.

(D) Except during periods of system breakdowns, repairs, calibration checks, and zero and span adjustments, the COMS must be in continuous operation and must complete a minimum of one cycle of sampling and analyzing for each successive 10 second period and one cycle of data recording for each successive 6-minute period.

(E) You must reduce all data from the COMS to 6-minute averages. Six-minute opacity averages must be calculated from 36 or more data points equally spaced over each 6-minute period. Data recorded during periods of system breakdowns, repairs, calibration checks, and zero and span adjustments must not be included in the data averages. An arithmetic or integrated average of all data may be used.

(iii) During each performance test conducted according to paragraph (o)(1) of this section, you must establish an opacity baseline level. The value of the opacity baseline level is determined by averaging all of the 6-minute average opacity values (reported to the nearest 0.1 percent opacity) from the COMS measurements recorded during each of the test run intervals conducted for the performance test, and then adding 2.5 percent opacity to your calculated average opacity value for all of the test runs. If your calculated average opacity value for all of the test runs is less than 5.0 percent, then the opacity baseline level is set at 5.0 percent.

(iv) You must evaluate the preceding 24-hour average opacity level measured by the COMS each boiler operating day excluding periods of affected source startup, shutdown, or malfunction. If the measured 24-hour average opacity emission level is greater than the baseline opacity level determined in paragraph (o)(2)(iii) of this section, you must initiate investigation of the relevant equipment and control systems within 24 hours of the first discovery of the high opacity incident and take the appropriate corrective action as soon as practicable to adjust control settings or repair equipment to reduce the measured 24-hour average opacity to a level below the baseline opacity level.

(v) You must record the opacity measurements, calculations performed, and any corrective actions taken. The record of corrective action taken must include the date and time during which the measured 24-hour average opacity was greater than baseline opacity level, and the date, time, and description of the corrective action.

(vi) If the measured 24-hour average opacity for your affected source remains at a level greater than the opacity baseline level after 7 days, then you must conduct a new PM performance test according to paragraph (o)(1) of this section and establish a new opacity baseline value according to paragraph (o)(2) of this section. This new performance test must be conducted within 60 days of the date that the measured 24-hour average opacity was first determined to exceed the baseline opacity level unless a wavier is granted by the appropriate delegated permitting authority.

(3) As an alternative to complying with the requirements of paragraph (o)(2) of this section, an owner or operator may elect to monitor the performance of an electrostatic precipitator (ESP) operated to comply with the applicable PM emissions limit in §60.42Da(c)(2) or (d) using an ESP predictive model developed in accordance with the requirements in paragraphs (o)(3)(i) through (v) of this section.

(i) You must calibrate the ESP predictive model with each PM control device used to comply with the applicable PM emissions limit in §60.42Da(c)(2) or (d) *operating under normal conditions*. In cases when a wet scrubber is used in combination with an ESP to comply with the PM emissions limit, the daily average liquid-to-gas flow rate for the wet scrubber must be maintained at 90 percent of average ratio measured during all test run intervals for the performance test conducted according to paragraph (o)(1) of this section.

(ii) You must develop a site-specific monitoring plan that includes a description of the ESP predictive model used, the model input parameters, and the procedures and criteria for establishing monitoring parameter baseline levels indicative of compliance with the PM emissions limit. You must submit the site-specific monitoring plan for approval by the appropriate delegated permitting authority. For reference purposes in preparing the monitoring plan, see the OAQPS "Compliance Assurance *Monitoring (CAM) Protocol for an Electrostatic Precipitator* (ESP) Controlling Particulate Matter (PM) Emissions from a Coal-Fired Boiler." This document is available from the U.S. Environmental Protection Agency (U.S. EPA); Office of Air Quality Planning and Standards; Sector Policies and Programs Division; Measurement Policy Group (D243–02), Research Triangle Park, NC 27711. This document is also available on the Technology Transfer Network (TTN) under Emission Measurement Center Continuous Emission Monitoring .

(iii) You must run the ESP predictive model using the applicable input data each boiler operating day and evaluate the model output for the preceding boiler operating day excluding periods of affected source startup, shutdown, or malfunction. If the values for one or more of the model parameters exceed the applicable baseline levels determined according to your approved site-specific monitoring plan, you must initiate investigation of the relevant equipment and control systems within 24 hours of the first discovery of a model parameter deviation and, take the *appropriate corrective action as soon as practicable to adjust* control settings or repair equipment to return the model output to within the applicable baseline levels.

(iv) You must record the ESP predictive model inputs and outputs and any corrective actions taken. The record of corrective action taken must include the date and time during which the model output values exceeded the applicable baseline levels, and the date, time, and description of the corrective action.

(v) If after 7 consecutive days a model parameter continues to exceed the applicable baseline level, then you must conduct a *new PM performance test according to paragraph (o)(1) of this* section. This new performance test must be conducted within 60 days of the date that the model parameter was first determined to exceed its baseline level unless a wavier is granted by the appropriate delegated permitting authority.

(4) As an alternative to complying with the requirements of paragraph (o)(2) of this section, an owner or operator may elect to monitor the performance of a fabric filter (baghouse) operated to comply with the applicable PM emissions limit in §60.42Da(c)(2) or (d) by using a bag leak detection system according to the requirements in paragraphs (o)(4)(i) through (v) of this section.

(i) Each bag leak detection system must meet the specifications and requirements in paragraphs (o)(4)(i)(A) through (H) of this section.

(A) The bag leak detection system must be certified by the *manufacturer* to be capable of detecting PM emissions at concentrations of 1 milligram per actual cubic meter (0.00044 grains per actual cubic foot) or less.

(B) The bag leak detection system sensor must provide output of relative PM loadings. The owner or operator must continuously record the output from the bag leak detection system using electronic or other means (*e.g.* , using a strip chart recorder or a data logger.)

(C) The bag leak detection system must be equipped with an alarm system that will react when the system detects an increase in relative particulate loading over the alarm set point established according to paragraph (o)(4)(i)(D) of this section, and the alarm must be located such that it can be noticed by the appropriate plant personnel.

(D) In the initial adjustment of the bag leak detection system, you must establish, at a minimum, the baseline output by adjusting the sensitivity (range) and the averaging period of the device, the alarm set points, and the alarm delay time.

(E) Following initial adjustment, you must not adjust the averaging period, alarm set point, or alarm delay time without approval from the appropriate delegated permitting authority except as provided in paragraph (d)(1)(vi) of this section.

(F) Once per quarter, you may adjust the sensitivity of the bag leak detection system to account for seasonal effects, including temperature and humidity, according to the procedures identified in the site-specific monitoring plan required by paragraph (o)(4)(ii) of this section.

(G) You must install the bag leak detection sensor downstream of the fabric filter and upstream of any wet scrubber.

(H) Where multiple detectors are required, the system's instrumentation and alarm may be shared among detectors.

(ii) You must develop and submit to the appropriate delegated permitting authority for approval a site-specific monitoring plan for each bag leak detection system. You must operate and maintain the bag leak detection system according to the site-specific monitoring plan at all times. Each monitoring plan must describe the items in paragraphs (o)(4)(ii)(A) through (F) of this section.

(A) Installation of the bag leak detection system;

(B) Initial and periodic adjustment of the bag leak detection system, including how the alarm set-point will be established;

(C) Operation of the bag leak detection system, including quality assurance procedures;

(D) How the bag leak detection system will be maintained, including a routine maintenance schedule and spare parts inventory list;

(E) How the bag leak detection system output will be recorded and stored; and

(F) Corrective action procedures as specified in paragraph (o)(4)(iii) of this section. In approving the site-specific monitoring plan, the appropriate delegated permitting authority may allow owners and operators more than 3 hours to alleviate a specific condition that causes an alarm if the owner or operator identifies in the monitoring plan this specific condition as one that could lead to an alarm, adequately explains why it is not feasible to alleviate this condition within 3 hours of the time the alarm occurs, and demonstrates that the requested time will ensure alleviation of this condition as expeditiously as practicable.

(iii) For each bag leak detection system, you must initiate procedures to determine the cause of every alarm within 1 hour of the alarm. Except as provided in paragraph (o)(4)(ii)(F) of this section, you must alleviate the cause of the alarm within 3 hours of the alarm by taking whatever corrective action(s) are necessary. Corrective actions may include, but are not limited to the following:

(A) Inspecting the fabric filter for air leaks, torn or broken bags or filter media, or any other condition that may cause an increase in particulate emissions;

(B) Sealing off defective bags or filter media;

(C) Replacing defective bags or filter media or otherwise repairing the control device;

(D) Sealing off a defective fabric filter compartment;

(E) Cleaning the bag leak detection system probe or otherwise repairing the bag leak detection system; or

(F) Shutting down the process producing the particulate emissions.

(iv) You must maintain records of the information specified in paragraphs (o)(4)(iv)(A) through (C) of this section for each bag leak detection system.

(A) Records of the bag leak detection system output;

(B) Records of bag leak detection system adjustments, including the date and time of the adjustment, the initial bag leak detection system settings, and the final bag leak detection system settings; and

(C) The date and time of all bag leak detection system alarms, the time that procedures to determine the cause of the alarm were initiated, if procedures were initiated within 1 hour of the alarm, the cause of the alarm, an explanation of the actions taken, the date and time the cause of the alarm was alleviated, and if the alarm was alleviated within 3 hours of the alarm.

(v) If after any period of composed of 30 boiler operating days during which the alarm rate exceeds 5 percent of the process operating time (excluding control device or process startup, shutdown, and malfunction), then you must conduct a new PM performance test according to paragraph (o)(1) of this section. This new performance test must be conducted within 60 days of the date that the alarm rate was first determined to exceed 5 percent limit unless a wavier is granted by the appropriate delegated permitting authority.

(5) An owner or operator of a modified affected source electing to meet the emission limitations in §.42Da(d) shall determine the percent reduction in PM by using the emission rate for PM determined by the performance test conducted according to the requirements in paragraph (o)(1) of this section and the ash content on a mass basis of the fuel burned during each performance test run as determined by analysis of the fuel as fired.

(p) As an alternative to meeting the compliance provisions specified in paragraph (o) of this section, an owner or operator may elect to install, certify, maintain, and operate a CEMS measuring PM emissions discharged from the affected facility to the atmosphere and record the output of the system as specified in paragraphs (p)(1) through (p)(8) of this section.

(1) The owner or operator shall submit a written notification to the Administrator of intent to demonstrate compliance with this subpart by using a CEMS measuring PM. This notification shall be sent at least 30 calendar days before the initial startup of the monitor for compliance determination purposes. The owner or operator may discontinue operation of the monitor and instead return to demonstration of compliance with this subpart according to the requirements in paragraph (o) of this section by submitting written notification to the Administrator of such intent at least 30 calendar days before shutdown of the monitor for compliance determination purposes.

(2) Each CEMS shall be installed, certified, operated, and maintained according to the requirements in §60.49Da(v).

(3) The initial performance evaluation shall be completed no later than 180 days after the date of initial startup of the affected facility, as specified under §60.8 of subpart A of this part or within 180 days of the date of notification to the Administrator required under paragraph (p)(1) of this section, whichever is later.

(4) Compliance with the applicable emissions limit shall be determined based on the 24-hour daily (block) average of the hourly arithmetic average emissions concentrations using the continuous monitoring system outlet data. The 24-hour block arithmetic average emission concentration shall be calculated using EPA Reference Method 19 of appendix A of this part, section 4.1.

(5) At a minimum, valid CEMS hourly averages shall be obtained for 75 percent of all operating hours on a 30-day rolling average basis. Beginning on January 1, 2012, valid CEMS hourly averages shall be obtained for 90 percent of all operating hours on a 30-day rolling average basis.

(i) At least two data points per hour shall be used to calculate each 1-hour arithmetic average.

(ii) [Reserved]

(6) The 1-hour arithmetic averages required shall be expressed in ng/J, MMBtu/hr, or lb/MWh and shall be used to calculate the boiler operating day daily arithmetic average emission concentrations. The 1-hour arithmetic averages shall be calculated using the data points required under §60.13(e)(2) of subpart A of this part.

(7) All valid CEMS data shall be used in calculating average emission concentrations even if the minimum CEMS data requirements of paragraph (j)(5) of this section are not met.

(8) When PM emissions data are not obtained because of CEMS breakdowns, repairs, calibration checks, and zero and span adjustments, emissions data shall be obtained by using other monitoring systems as approved by the Administrator or EPA Reference Method 19 of appendix A of this part to provide, as necessary, valid emissions data for a minimum of 90 percent (only 75 percent is required prior to January 1, 2012) of all operating hours per 30-day rolling average.

§ 60.49Da Emission monitoring.

(a) Except as provided for in paragraphs (t) and (u) of this section, the owner or operator of an affected facility, shall install, calibrate, maintain, and operate a CEMS, and record the output of the system, for measuring the opacity of emissions discharged to the atmosphere. If opacity interference due to water droplets exists in the stack (for example, from the use of an FGD system), the opacity is monitored upstream of the interference (at the inlet to the FGD system). If opacity interference is experienced at all locations (both at the inlet and outlet of the SO_2control system), alternate parameters indicative of the PM control system's performance and/or good combustion are monitored (subject to the approval of the Administrator).

(b) The owner or operator of an affected facility shall install, calibrate, maintain, and operate a CEMS, and record the output of the system, for measuring SO_2emissions, except where natural gas is the only fuel combusted, as follows:

(1) Sulfur dioxide emissions are monitored at both the inlet and outlet of the SO_2control device.

(2) For a facility that qualifies under the numerical limit provisions of §60.43Da(d), (i), (j), or (k) SO_2emissions are only monitored as discharged to the atmosphere.

(3) An "as fired" fuel monitoring system (upstream of coal pulverizers) meeting the requirements of Method 19 of appendix A of this part may be used to determine potential SO_2emissions in place of a continuous SO_2emission monitor at the inlet to the SO_2control device as required under paragraph (b)(1) of this section.

(4) If the owner or operator has installed and certified a SO_2continuous emissions monitoring system (CEMS) according to the requirements of §75.20(c)(1) of this chapter and appendix A to part 75 of this chapter, and is continuing to meet the ongoing quality assurance requirements of §75.21 of this chapter and appendix B to part 75 of this chapter, that CEMS may be used to meet the requirements of this section, provided that:

(i) A CO_2or O_2continuous monitoring system is installed, calibrated, maintained and operated at the same location, according to paragraph (d) of this section; and

(ii) For sources subject to an SO_2emission limit in lb/MMBtu under §60.43Da:

(A) When relative accuracy testing is conducted, SO_2concentration data and CO_2(or O_2) data are collected simultaneously; and

(B) In addition to meeting the applicable $SO_2$and CO_2(or O_2) relative accuracy specifications in Figure 2 of appendix B to part 75 of this chapter, the relative accuracy (RA) standard in section 13.2 of Performance Specification 2 in appendix B to this part is met when the RA is calculated on a lb/MMBtu basis; and

(iii) The reporting requirements of §60.51Da are met. The $SO_2$and CO_2(or O_2) data reported to meet the requirements of §60.51Da shall not include substitute data values derived from the missing data procedures in subpart D of part 75 of this chapter, nor shall the SO_2data have been bias adjusted according to the procedures of part 75 of this chapter.

(c)(1) The owner or operator of an affected facility shall install, calibrate, maintain, and operate a CEMS, and record the output of the system, for measuring NO_Xemissions discharged to the atmosphere; or

(2) If the owner or operator has installed a NO_Xemission rate CEMS to meet the requirements of part 75 of this chapter and is continuing to meet the ongoing requirements of part 75 of this chapter, that CEMS may be used to meet the requirements of this section, except that the owner or operator shall also meet the *requirements* of §60.51Da. Data reported to meet the requirements of §60.51Da shall not include data substituted using the missing data procedures in subpart D of part 75 of this chapter, nor shall the data have been bias adjusted according to the procedures of part 75 of this chapter.

(d) *The owner or operator of an affected facility shall install,* calibrate, maintain, and operate a CEMS, and record the output of the system, for measuring the O_2or carbon dioxide (CO_2) content of the flue gases at each location where SO_2or NO_Xemissions are monitored. For affected facilities subject to a lb/MMBtu SO_2emission limit under §60.43Da, if the owner or operator has installed and certified a CO_2or O_2monitoring system according to §75.20(c) of this chapter and Appendix A to part 75 of this chapter and the monitoring system continues to meet the applicable quality-assurance provisions of §75.21 of this chapter and appendix B to part 75 of this chapter, that CEMS may be used together with the part 75 SO_2concentration monitoring system described in paragraph (b) of this section, to determine the SO_2emission rate in lb/MMBtu. SO_2data used to meet the requirements of §60.51Da shall not include substitute data values derived from the *missing data procedures in subpart D of part 75 of this chapter, nor* shall the data have been bias adjusted according to the procedures of part 75 of this chapter.

(e) The CEMS under paragraphs (b), (c), and (d) of this section are operated and data recorded during all periods of operation of the affected facility including periods of startup, shutdown, malfunction or emergency conditions, except for CEMS breakdowns, repairs, calibration checks, and zero and span adjustments.

(f)(1) For units that began construction, reconstruction, or modification on or before February 28, 2005, the owner or operator shall obtain emission data for at least 18 hours in at least 22 out of 30 successive boiler operating days. If this minimum data requirement cannot be met with CEMS, the owner or operator shall supplement emission data with other monitoring systems approved by the Administrator or the reference methods and procedures as described in paragraph (h) of this section.

(2) For units that began construction, reconstruction, or modification after February 28, 2005, the owner or operator shall obtain emission data for at least 90 percent of all operating hours for each 30 successive boiler operating days. If this minimum data requirement cannot be met with a CEMS, the owner or operator shall supplement emission data with other monitoring systems approved by the Administrator or the reference methods and procedures as described in paragraph (h) of this section.

(g) The 1-hour averages required under paragraph §60.13(h) are expressed in ng/J (lb/MMBtu) heat input and used to calculate the average emission rates under §60.48Da. The 1-hour averages are calculated using the data points required under §60.13(h)(2).

(h) When it becomes necessary to supplement CEMS data to meet the minimum data requirements in paragraph (f) of this section, the owner or operator shall use the reference methods and procedures as specified in this paragraph. Acceptable alternative methods and procedures are given in paragraph (j) of this section.

(1) Method 6 of appendix A of this part shall be used to determine the SO_2concentration at the same location as the SO_2monitor. Samples shall be taken at 60-minute intervals. The sampling time and sample volume for each sample shall be at least 20 minutes and 0.020 dscm (0.71 dscf). Each sample represents a 1-hour average.

(2) Method 7 of appendix A of this part shall be used to determine the NO_Xconcentration at the same location as the NO_Xmonitor. Samples shall be taken at 30-minute intervals. The arithmetic average of two consecutive samples represents a 1-hour average.

(3) The emission rate correction factor, integrated bag sampling and analysis procedure of Method 3B of appendix A of this part shall be used to determine the O_2or CO_2concentration at the same location as the O_2or CO_2monitor. Samples shall be taken for at least 30 minutes in each hour. Each sample represents a 1-hour average.

(4) The procedures in Method 19 of appendix A of this part shall be used to compute each 1-hour average concentration in ng/J (lb/MMBtu) heat input.

(i) The owner or operator shall use methods and procedures in this paragraph to conduct monitoring system performance evaluations under §60.13(c) and calibration checks under §60.13(d). Acceptable alternative methods and procedures are given in paragraph (j) of this section.

(1) Methods 3B, 6, and 7 of appendix A of this part shall be used to determine O_2, SO_2, and NO_Xconcentrations, respectively.

(2) SO_2or NO_X(NO), as applicable, shall be used for preparing the calibration gas mixtures (in N_2, as applicable) under Performance Specification 2 of appendix B of this part.

(3) For affected facilities burning only fossil fuel, the span value for a CEMS for measuring opacity is between 60 and 80 percent. Span values for a CEMS measuring NO_Xshall be determined using one of the following procedures:

(i) Except as provided under paragraph (i)(3)(ii) of this section, NO_Xspan values shall be determined as follows:

Fossil fuel	Span values for NO_X (ppm)
Gas	500.
Liquid	500.
Solid	1,000.
Combination	500 (x + y) + 1,000z.

Where:

x = Fraction of total heat input derived from gaseous fossil fuel,

y = Fraction of total heat input derived from liquid fossil fuel, and

z = Fraction of total heat input derived from solid fossil fuel.

(ii) As an alternative to meeting the requirements of paragraph (i)(3)(i) of this section, the owner or operator of an affected facility may elect to use the NO_Xspan values determined according to section 2.1.2 in appendix A to part 75 of this chapter.

(4) All span values computed under paragraph (i)(3)(i) of this section for burning combinations of fossil fuels are rounded to the nearest 500 ppm. Span values computed under paragraph (i)(3)(ii) of this section shall be rounded off according to section 2.1.2 in appendix A to part 75 of this chapter.

(5) For affected facilities burning fossil fuel, alone or in combination with non-fossil fuel and determining span values under paragraph (i)(3)(i) of this section, the span value of the SO_2CEMS at the inlet to the SO_2control device is 125 percent of the maximum estimated hourly potential emissions of the fuel fired, and the outlet of the SO_2control device is 50 percent of maximum estimated hourly potential emissions of the fuel fired. For affected facilities determining span values under paragraph (i)(3)(ii) of this section, SO_2span values shall be determined according to section 2.1.1 in appendix A to part 75 of this chapter.

(j) The owner or operator may use the following as alternatives to the reference methods and procedures specified in this section:

(1) For Method 6 of appendix A of this part, Method 6A or 6B (whenever Methods 6 and 3 or 3B of appendix A of this part data are used) or 6C of appendix A of this part may be used. Each Method 6B of appendix A of this part sample obtained over 24 hours represents 24 1-hour averages. If Method 6A or 6B of appendix A of this part is used under paragraph (i) of this section, the conditions under §60.48Da(d)(1) apply; these conditions do not apply under paragraph (h) of this section.

(2) For Method 7 of appendix A of this part, Method 7A, 7C, 7D, or 7E of appendix A of this part may be used. If Method 7C, 7D, or 7E of appendix A of this part is used, the sampling time for each run shall be 1 hour.

(3) For Method 3 of appendix A of this part, Method 3A or 3B of appendix A of this part may be used if the sampling time is 1 hour.

(4) For Method 3B of appendix A of this part, Method 3A of appendix A of this part may be used.

(k) The procedures specified in paragraphs (k)(1) through (3) of this section shall be used to determine gross output for sources demonstrating compliance with the output-based standard under §60.44Da(d)(1).

(1) The owner or operator of an affected facility with electricity generation shall install, calibrate, maintain, and operate a wattmeter; measure gross electrical output in MWh on a continuous basis; and record the output of the monitor.

(2) The owner or operator of an affected facility with process steam generation shall install, calibrate, maintain, and operate meters for steam flow, temperature, and pressure; measure gross process steam output in joules per hour (or Btu per hour) on a continuous basis; and record the output of the monitor.

(3) For affected facilities generating process steam in combination with electrical generation, the gross energy output is determined from the gross electrical output measured in accordance with paragraph (k)(1) of this section plus 75 percent of the gross thermal output (measured relative to ISO conditions) of the process steam measured in accordance with paragraph (k)(2) of this section.

(l) The owner or operator of an affected facility demonstrating compliance with an output-based standard under §60.42Da, §60.43Da, §60.44Da, or §60.45Da shall install, certify, operate, and maintain a continuous flow monitoring system meeting the requirements of Performance Specification 6 of appendix B of this part and the CD assessment, RATA and reporting provisions of procedure 1 of appendix F of this part, and record the output of the system, for measuring the volumetric flow rate of exhaust gases discharged to the atmosphere; or

(m) Alternatively, data from a continuous flow monitoring system certified according to the requirements of §75.20(c) of this chapter and appendix A to part 75 of this chapter, and continuing to meet the applicable quality control and quality assurance requirements of §75.21 of this chapter and appendix B to part 75 of this chapter, may be used. Flow rate data reported to meet the requirements of §60.51Da shall not include substitute data values derived from the missing data procedures in subpart D of part 75 of this chapter, nor shall the data have been bias adjusted according to the procedures of part 75 of this chapter.

(n) Gas-fired and oil-fired units. The owner or operator of an affected unit that qualifies as a gas-fired or oil-fired unit, as defined in 40 CFR 72.2, may use, as an alternative to the requirements specified in either paragraph (l) or (m) of this section, a fuel flow monitoring system certified and operated according to the requirements of appendix D of part 75 of this chapter.

(o) The owner or operator of a duct burner, as described in §60.41Da, which is subject to the NO_Xstandards of §60.44Da(a)(1), (d)(1), or (e)(1) is not required to install or operate a CEMS to measure NO_Xemissions; a wattmeter to measure gross electrical output; meters to measure steam flow, temperature, and pressure; and a continuous flow monitoring system to measure the flow of exhaust gases discharged to the atmosphere.

(p) The owner or operator of an affected facility demonstrating compliance with an Hg limit in §60.45Da shall install and operate a CEMS to measure and record the concentration of Hg in the exhaust gases from each stack according to the requirements in paragraphs (p)(1) through (p)(3) of this section. Alternatively, for an affected facility that is also subject to the requirements of subpart I of part 75 of this chapter, the owner or operator may install, certify, maintain, operate and quality-assure the data from a Hg CEMS according to §75.10 of this chapter and appendices A and B to part 75 of this chapter, in lieu of following the procedures in paragraphs (p)(1) through (p)(3) of this section.

(1) The owner or operator must install, operate, and maintain each CEMS according to Performance Specification 12A in appendix B to this part.

(2) The owner or operator must conduct a performance evaluation of each CEMS according to the requirements of §60.13 and Performance Specification 12A in appendix B to this part.

(3) The owner or operator must operate each CEMS according to the requirements in paragraphs (p)(3)(i) through (iv) of this section.

(i) As specified in §60.13(e)(2), each CEMS must complete a minimum of one cycle of operation (sampling, analyzing, and data recording) for each successive 15-minute period.

(ii) The owner or operator must reduce CEMS data as specified in §60.13(h).

(iii) The owner or operator shall use all valid data points collected during the hour to calculate the hourly average Hg concentration.

(iv) The owner or operator must record the results of each required certification and quality assurance test of the CEMS.

(4) Mercury CEMS data collection must conform to paragraphs (p)(4)(i) through (iv) of this section.

(i) For each calendar month in which the affected unit operates, valid hourly Hg concentration data, stack gas volumetric flow rate data, moisture data (if required), and electrical output data (i.e., valid data for all of these parameters) shall be obtained for at least 75 percent of the unit operating hours in the month.

(ii) Data reported to meet the requirements of this subpart shall not include hours of unit startup, shutdown, or malfunction. In addition, for an affected facility that is also subject to subpart I of part 75 of this chapter, data reported to meet the requirements of this subpart shall not include data substituted using the missing data procedures in subpart D of part 75 of this chapter, nor shall the data have been bias adjusted according to the procedures of part 75 of this chapter.

(iii) If valid data are obtained for less than 75 percent of the unit operating hours in a month, you must discard the data collected in that month and replace the data with the mean of the individual monthly emission rate values determined in the last 12 months. In the 12-month rolling average calculation, this substitute Hg emission rate shall be weighted according to the number of unit operating hours in the month for which the data capture requirement of §60.49Da(p)(4)(i) was not met.

(iv) Notwithstanding the requirements of paragraph (p)(4)(iii) of this section, if valid data are obtained for less than 75 percent of the unit operating hours in another month in that same 12-month rolling average cycle, discard the data collected in that month and replace the data with the highest individual monthly emission rate determined in the last 12 months. In the 12-month rolling average calculation, this substitute Hg emission rate shall be weighted according to the number of unit operating hours in the month for which the data capture requirement of §60.49Da(p)(4)(i) was not met.

(q) As an alternative to the CEMS required in paragraph (p) of this section, the owner or operator may use a sorbent trap monitoring system (as defined in §72.2 of this chapter) to monitor Hg concentration, according to the procedures described in §75.15 of this chapter and appendix K to part 75 of this chapter.

(r) For Hg CEMS that measure Hg concentration on a dry basis or for sorbent trap monitoring systems, the emissions data must be corrected for the stack gas moisture content. A certified continuous moisture monitoring system that meets the requirements of §75.11(b) of this chapter is acceptable for this purpose. Alternatively, the appropriate default moisture value, as specified in §75.11(b) or §75.12(b) of this chapter, may be used.

(s) The owner or operator shall prepare and submit to the Administrator for approval a unit-specific monitoring plan for each monitoring system, at least 45 days before commencing certification testing of the monitoring systems. The owner or operator shall comply with the requirements in your plan. The plan must address the requirements in paragraphs (s)(1) through (6) of this section.

(1) Installation of the CEMS sampling probe or other interface at a measurement location relative to each affected process unit such that the measurement is representative of the exhaust emissions (*e.g.* , on or downstream of the last control device);

(2) Performance and equipment specifications for the sample interface, the pollutant concentration or parametric signal analyzer, and the data collection and reduction systems;

(3) Performance evaluation procedures and acceptance criteria (*e.g.,* calibrations, relative accuracy test audits (RATA), etc.);

(4) Ongoing operation and maintenance procedures in accordance with the general requirements of §60.13(d) or part 75 of this chapter (as applicable);

(5) Ongoing data quality assurance procedures in accordance with the general requirements of §60.13 or part 75 of this chapter (as applicable); and

(6) Ongoing recordkeeping and reporting procedures in accordance with the requirements of this subpart.

(t) The owner or operator of an affected facility demonstrating compliance with the output-based emissions limitation under §60.42Da(c)(1) shall install, certify, operate, and maintain a CEMS for measuring PM emissions according to the requirements of paragraph (v) of this section. An owner or operator of an affected source demonstrating compliance with the input-based emission limitation under §60.42Da(c)(2) may install, certify, operate, and maintain a CEMS for measuring PM emissions according to the requirements of paragraph (v) of this section.

(u) An owner or operator of an affected source that meets the conditions in either paragraph (u)(1), (2) or (3) of this section is exempted from the continuous opacity monitoring system requirements in paragraph (a) of this section and the monitoring requirements in §60.48Da(o).

(1) A CEMS for measuring PM emissions is used to demonstrate continuous compliance on a boiler operating day average with the emissions limitations under §60.42Da(a)(1) or §60.42Da(c)(2) and is installed, certified, operated, and maintained on the affected source according to the requirements of paragraph (v) of this section; or

(2) The affected source burns only gaseous fuels and does not use a post-combustion technology to reduce emissions of SO_2or PM; or

(3) The affected source does not use post-combustion technology (except a wet scrubber) for reducing PM, SO_2, or carbon monoxide

(CO) emissions, burns only natural gas, gaseous fuels, or fuel oils that contain less than or equal to 0.30 weight percent sulfur, and is operated such that emissions of CO to the atmosphere from the affected source are maintained at levels less than or equal to 1.4 lb/MWh on a boiler operating day average basis. Owners and operators of affected sources electing to comply with this paragraph must demonstrate compliance according to the procedures specified in paragraphs (u)(3)(i) through (iv) of this section.

(i) You must monitor CO emissions using a CEMS according to the procedures specified in paragraphs (u)(3)(i)(A) through (D) of this section.

(A) The CO CEMS must be installed, certified, maintained, and operated according to the provisions in §60.58b(i)(3) of subpart Eb of this part.

(B) Each 1-hour CO emissions average is calculated using the data points generated by the CO CEMS expressed in parts per million by volume corrected to 3 percent oxygen (dry basis).

(C) At a minimum, valid 1-hour CO emissions averages must be obtained for at least 90 percent of the operating hours on a 30-day rolling average basis. At least two data points per hour must be used to calculate each 1-hour average.

(D) Quarterly accuracy determinations and daily calibration drift tests for the CO CEMS must be performed in accordance with procedure 1 in appendix F of this part.

(ii) You must calculate the 1-hour average CO emissions levels for each boiler operating day by multiplying the average hourly CO output concentration measured by the CO CEMS times the corresponding average hourly flue gas flow rate and divided by the corresponding average hourly useful energy output from the affected source. The 24-hour average CO emission level is determined by calculating the arithmetic average of the hourly CO emission levels computed for each boiler operating day.

(iii) You must evaluate the preceding 24-hour average CO emission level each boiler operating day excluding periods of affected source startup, shutdown, or malfunction. If the 24-hour average CO emission level is greater than 1.4 lb/MWh, you must initiate investigation of the relevant equipment and control systems within 24 hours of the first discovery of the high emission incident and, take the appropriate corrective action as soon as practicable to adjust control settings or repair equipment to reduce the 24-hour average CO emission level to 1.4 lb/MWh or less.

(iv) You must record the CO measurements and calculations performed according to paragraph (u)(3) of this section and any corrective actions taken. The record of corrective action taken must include the date and time during which the 24-hour average CO emission level was greater than 1.4 lb/MWh, and the date, time, and description of the corrective action.

(v) The owner or operator of an affected facility using a CEMS measuring PM emissions to meet requirements of this subpart shall install, certify, operate, and maintain the CEMS as specified in paragraphs (v)(1) through (v)(3).

(1) The owner or operator shall conduct a performance evaluation of the CEMS according to the applicable requirements of §60.13, Performance Specification 11 in appendix B of this part, and procedure 2 in appendix F of this part.

(2) During each relative accuracy test run of the CEMS required by Performance Specification 11 in appendix B of this part, PM and O_2(or CO_2) data shall be collected concurrently (or within a 30-to 60-minute period) by both the CEMS and conducting performance tests using the following test methods.

(i) For PM, EPA Reference Method 5, 5B, or 17 of appendix A of this part shall be used.

(ii) For O_2(or CO_2), EPA Reference Method 3, 3A, or 3B of appendix A of this part, as applicable shall be used.

(3) Quarterly accuracy determinations and daily calibration drift tests shall be performed in accordance with procedure 2 in appendix F of this part. Relative Response Audit's must be performed annually and Response Correlation Audits must be performed every 3 years.

(w)(1) Except as provided for under paragraphs (w)(2), (w)(3), and (w)(4) of this section, the SO_2, NO_X, CO_2, and O_2CEMS required under paragraphs (b) through (d) of this section shall be installed, certified, and operated in accordance with the applicable procedures in Performance Specification 2 or 3 in appendix B to this part or according to the procedures in appendices A and B to part 75 of this chapter. Daily calibration drift assessments and quarterly accuracy determinations shall be done in accordance with Procedure 1 in appendix F to this part, and a data assessment report (DAR), prepared according to section 7 of Procedure 1 in appendix F to this part, shall be submitted with each compliance report required under §60.51Da., the owner or operator may elect to implement the following alternative data accuracy assessment procedures:

(2) As an alternative to meeting the requirements of paragraph (w)(1) of this section, an owner or operator may elect to may elect to implement the following alternative data accuracy assessment procedures. For all required $CO_2$and O_2CEMS and for $SO_2$and NO_xCEMS with span values greater than 100 ppm, the daily calibration error test and calibration adjustment procedures described in sections 2.1.1 and 2.1.3 of appendix B to part 75 of this chapter may be followed instead of the CD assessment procedures in Procedure 1, section 4.1 of appendix F of this part. If this option is selected, the data validation and out-of-control provisions in sections 2.1.4 and 2.1.5 of appendix B to part 75 of this chapter shall be followed instead of the excessive CD and out-of-control criteria in Procedure 1, section 4.3 of appendix F to this part. For the purposes of data validation under this subpart, the excessive CD and out-of-control criteria in Procedure 1, section 4.3 of appendix F to this part shall apply to $SO_2$and NO_xspan values less than 100 ppm;

(3) As an alternative to meeting the requirements of paragraph (w)(1) of this section, an owner or operator may elect to may elect to implement the following alternative data accuracy assessment procedures. For all required $CO_2$and O_2CEMS and for $SO_2$and NO_xCEMS with span values greater than 30 ppm, quarterly linearity checks may be performed in accordance with section 2.2.1 of appendix B to part 75 of this chapter, instead of performing the cylinder gas audits (CGAs) described in Procedure 1, section 5.1.2 of appendix F to this part. If this option is selected: The frequency of the linearity checks shall be as specified in section 2.2.1 of appendix B to part 75 of this chapter; the applicable linearity specifications in section 3.2 of appendix A to part 75 of this chapter shall be met; the data validation and out-of-control criteria in section 2.2.3 of appendix B to part 75 of this chapter shall be followed instead of the excessive audit inaccuracy and out-of-control criteria in Procedure 1, section 5.2 of appendix F to this part; and the grace period provisions in section 2.2.4 of appendix B to part 75 of this chapter shall apply. For the purposes of data validation under this subpart, the cylinder gas audits described in Procedure 1, section 5.1.2 of appendix F to this part shall be performed for $SO_2$and NO_xspan values less than or equal to 30 ppm;

(4) As an alternative to meeting the requirements of paragraph (w)(1) of this section, an owner or operator may elect to may elect to implement the following alternative data accuracy assessment procedures. For SO_2, CO_2, and O_2CEMS and for NO_xCEMS, RATAs may be performed in accordance with section 2.3 of appendix B to part 75 of this chapter instead of following the procedures described in Procedure 1, section 5.1.1 of appendix F to this part. If this option is selected: The frequency of each RATA shall be as specified in section

2.3.1 of appendix B to part 75 of this chapter; the applicable relative accuracy specifications shown in Figure 2 in appendix B to part 75 of this chapter shall be met; the data validation and out-of-control criteria in section 2.3.2 of appendix B to part 75 of this chapter shall be followed instead of the excessive audit inaccuracy and out-of-control criteria in Procedure 1, section 5.2 of appendix F to this part; and the grace period provisions in section 2.3.3 of appendix B to part 75 of this chapter shall apply. For the purposes of data validation under this subpart, the relative accuracy specification in section 13.2 of Performance Specification 2 in appendix B to this part shall be met on a lb/MMBtu basis for SO_2 (regardless of the SO_2 emission level during the RATA), and for NO_X when the average NO_X emission rate measured by the reference method during the RATA is less than 0.100 lb/MMBtu;

(5) If the owner or operator elects to implement the alternative data assessment procedures described in paragraphs (w)(2) through (w)(4) of this section, each data assessment report shall include a summary of the results of all of the RATAs, linearity checks, CGAs, and calibration error or drift assessments required by paragraphs (w)(2) through (w)(4) of this section.

§ 60.50Da Compliance determination procedures and methods.

(a) In conducting the performance tests required in §60.8, the owner or operator shall use as reference methods and procedures the methods in appendix A of this part or the methods and procedures as specified in this section, except as provided in §60.8(b). Section 60.8(f) does not apply to this section for SO_2 and NO_X. Acceptable alternative methods are given in paragraph (e) of this section.

(b) The owner or operator shall determine compliance with the PM standards in §60.42Da as follows:

(1) The dry basis F factor (O_2) procedures in Method 19 of appendix A of this part shall be used to compute the emission rate of PM.

(2) For the particular matter concentration, Method 5 of appendix A of this part shall be used at affected facilities without wet FGD systems and Method 5B of appendix A of this part shall be used after wet FGD systems.

(i) The sampling time and sample volume for each run shall be at least 120 minutes and 1.70 dscm (60 dscf). The probe and filter holder heating system in the sampling train may be set to provide an average gas temperature of no greater than 160±14 °C (320±25 °F).

(ii) For each particulate run, the emission rate correction factor, integrated or grab sampling and analysis procedures of Method 3B of appendix A of this part shall be used to determine the O_2 concentration. The O_2 sample shall be obtained simultaneously with, and at the same traverse points as, the particulate run. If the particulate run has more than 12 traverse points, the O_2 traverse points may be reduced to 12 provided that Method 1 of appendix A of this part is used to locate the 12 O_2 traverse points. If the grab sampling procedure is used, the O_2 concentration for the run shall be the arithmetic mean of the sample O_2 concentrations at all traverse points.

(3) Method 9 of appendix A of this part and the procedures in §60.11 shall be used to determine opacity.

(c) The owner or operator shall determine compliance with the SO_2 standards in §60.43Da as follows:

(1) The percent of potential SO_2 emissions (%Ps) to the atmosphere shall be computed using the following equation:

$$\%P_s = \frac{(100 - \%R_f)(100 - \%R_g)}{100}$$

Where:

%Ps = Percent of potential SO_2 emissions, percent;

%Rf = Percent reduction from fuel pretreatment, percent; and

%Rg = Percent reduction by SO_2 control system, percent.

(2) The procedures in Method 19 of appendix A of this part may be used to determine percent reduction ($\%R_f$) of sulfur by such processes as fuel pretreatment (physical coal cleaning, hydrodesulfurization of fuel oil, etc.), coal pulverizers, and bottom and fly ash interactions. This determination is optional.

(3) The procedures in Method 19 of appendix A of this part shall be used to determine the percent SO_2 reduction ($\%R_g$) of any SO_2 control system. Alternatively, a combination of an "as fired" fuel monitor and emission rates measured after the control system, following the procedures in Method 19 of appendix A of this part, may be used if the percent reduction is calculated using the average emission rate from the SO_2 control device and the average SO_2 input rate from the "as fired" fuel analysis for 30 successive boiler operating days.

(4) The appropriate procedures in Method 19 of appendix A of this part shall be used to determine the emission rate.

(5) The CEMS in §60.49Da(b) and (d) shall be used to determine the concentrations of SO_2 and CO_2 or O_2.

(d) The owner or operator shall determine compliance with the NO_X standard in §60.44Da as follows:

(1) The appropriate procedures in Method 19 of appendix A of this part shall be used to determine the emission rate of NO_X.

(2) The continuous monitoring system in §60.49Da(c) and (d) shall be used to determine the concentrations of NO_X and CO_2 or O_2.

(e) The owner or operator may use the following as alternatives to the reference methods and procedures specified in this section:

(1) For Method 5 or 5B of appendix A of this part, Method 17 of appendix A of this part may be used at facilities with or without wet FGD systems if the stack temperature at the sampling location does not exceed an average temperature of 160 °C (320 °F). The procedures of §§2.1 and 2.3 of Method 5B of appendix A of this part may be used in Method 17 of appendix A of this part only if it is used after wet FGD systems. Method 17 of appendix A of this part shall not be used after wet FGD systems if the effluent is saturated or laden with water droplets.

(2) The F_c factor (CO_2) procedures in Method 19 of appendix A of this part may be used to compute the emission rate of PM under the stipulations of §60.46(d)(1). The CO_2 shall be determined in the same manner as the O_2 concentration.

(f) Electric utility combined cycle gas turbines are performance tested for PM, SO_2, and NO_X using the procedures of Method 19 of appendix A of this part. The SO_2 and NO_X emission rates from the gas turbine used in Method 19 of appendix A of this part calculations are determined when the gas turbine is performance tested under subpart

GG of this part. The potential uncontrolled PM emission rate from a gas turbine is defined as 17 ng/J (0.04 lb/MMBtu) heat input.

(g) For the purposes of determining compliance with the emission limits in §60.45Da, the owner or operator of an electric utility steam generating unit which is also a cogeneration unit shall use the procedures in paragraphs (g)(1) and (2) of this section to calculate emission rates based on electrical output to the grid plus 75 percent of the equivalent electrical energy (measured relative to ISO conditions) in the unit's process stream.

(1) All conversions from Btu/hr unit input to MW unit output must use equivalents found in 40 CFR 60.40(a)(1) for electric utilities (*i.e.* , 250 MMBtu/hr input to an electric utility steam generating unit is equivalent to 73 MW input to the electric utility steam generating unit); 73 MW input to the electric utility steam generating unit is equivalent to 25 MW output from the boiler electric utility steam generating unit; therefore, 250 MMBtu input to the electric utility steam generating unit is equivalent to 25 MW output from the electric utility steam generating unit).

(2) Use the Equation 5 in this section to determine the cogeneration Hg emission rate over a specific compliance period.

$$ER_{cogen} = \frac{M}{\left(V_{grid} + 0.75 \times V_{process}\right)} \qquad (\text{Eq. } 5)$$

Where:

ER_{cogen}= Cogeneration Hg emission rate over a compliance period in lb/MWh;

E = Mass of Hg emitted from the stack over the same compliance period (lb);

V_{grid}= Amount of energy sent to the grid over the same compliance period (MWh); and

$V_{process}$= Amount of energy converted to steam for process use over the same compliance period (MWh).

(h) The owner or operator shall determine compliance with the Hg limit in §60.45Da according to the procedures in paragraphs (h)(1) through (3) of this section.

(1) The initial performance test shall be commenced by the applicable date specified in §60.8(a). The required CEMS must be certified prior to commencing the test. The performance test consists of collecting hourly Hg emission data (lb/MWh) with the CEMS for 12 successive months of unit operation (excluding hours of unit startup, shutdown and malfunction). The average Hg emission rate is calculated for each month, and then the weighted, 12-month average Hg emission rate is calculated according to paragraph (h)(2) or (h)(3) of this section, as applicable. If, for any month in the initial performance test, the minimum data capture requirement in §60.49Da(p)(4)(i) is not met, the owner or operator shall report a substitute Hg emission rate for that month, as follows. For the first such month, the substitute monthly Hg emission rate shall be the arithmetic average of all valid hourly Hg emission rates recorded to date. For any subsequent month(s) with insufficient data capture, the substitute monthly Hg emission rate shall be the highest valid hourly Hg emission rate recorded to date. When the 12-month average Hg emission rate for the initial performance test is calculated, for each month in which there was insufficient data capture, the substitute monthly Hg emission rate shall be weighted according to the number of unit operating hours in that month. Following the initial performance test, the owner or operator shall demonstrate compliance by calculating the weighted average of all monthly Hg emission rates (in lb/MWh) for each 12 successive calendar months, excluding data obtained during startup, shutdown, or malfunction.

(2) If a CEMS is used to demonstrate compliance, follow the procedures in paragraphs (h)(2)(i) through (iii) of this section to determine the 12-month rolling average.

(i) Calculate the total mass of Hg emissions over a month (M), in lb, using either Equation 6 in paragraph (h)(2)(i)(A) of this section or Equation 7 in paragraph (h)(2)(i)(B) of this section, in conjunction with Equation 8 in paragraph (h)(2)(i)(C) of this section.

(A) If the Hg CEMS measures Hg concentration on a wet basis, use Equation 6 below to calculate the Hg mass emissions for each valid hour:

$$E_h = KC_h\,Q_h\,t_h \qquad (\text{Eq. } 6)$$

Where:

E_h= Hg mass emissions for the hour, (lb);

K = Units conversion constant, 6.24×10^{-11} lb-scm/µgm-scf;

C_h= Hourly $H_g$concentration, wet basis, (µgm/scm);

Q_h= Hourly stack gas volumetric flow rate, (scfh); and

t_h= Unit operating time, i.e., the fraction of the hour for which the unit operated. For example, th = 0.50 for a half-hour of unit operation and 1.00 for a full hour of operation.

(B) If the Hg CEMS measures Hg concentration on a dry basis, use Equation 7 below to calculate the Hg mass emissions for each valid hour:

$$E_h = KC_h\,Q_h\,t_h\,(1 - B_{ws}) \qquad (\text{Eq. } 7)$$

Where:

E_h= Hg mass emissions for the hour, (lb);

K = Units conversion constant, 6.24×10^{-11}lb-scm/µgm-scf;

C_h= Hourly Hg concentration, dry basis, (µgm/dscm);

Q_h= Hourly stack gas volumetric flow rate, (scfh);

t_h= Unit operating time, *i.e.* , the fraction of the hour for which the unit operated; and

B_{ws}= Stack gas moisture content, expressed as a decimal fraction (*e.g.* , for 8 percent H_2O, B_{ws}= 0.08).

(C) Use Equation 8, below, to calculate M, the total mass of Hg emitted for the month, by summing the hourly masses derived from Equation 6 or 7 (as applicable):

$$M = \sum_{h=1}^{n} E_h \qquad (\text{Eq. } 8)$$

Where:

M = Total Hg mass emissions for the month, (lb);

E_h= Hg mass emissions for hour "h", from Equation 6 or 7 of this section, (lb); and

n = Number of unit operating hours in the month with valid CE and electrical output data, excluding hours of unit startup, shutdown and malfunction.

(ii) Calculate the monthly Hg emission rate on an output basis (lb/MWh) using Equation 9, below. For a cogeneration unit, use Equation 5 in paragraph (g) of this section instead.

$$ER = \frac{M}{P} \qquad (Eq. 9)$$

Where:

ER = Monthly Hg emission rate, (lb/MWh);

M = Total mass of Hg emissions for the month, from Equation 8, above, (lb); and

P = Total electrical output for the month, for the hours used to calculate M, (MWh).

(iii) Until 12 monthly Hg emission rates have been accumulated, calculate and report only the monthly averages. Then, for each subsequent calendar month, use Equation 10 below to calculate the 12-month rolling average as a weighted average of the Hg emission rate for the current month and the Hg emission rates for the previous 11 months, with one exception. Calendar months in which the unit does not operate (zero unit operating hours) shall not be included in the 12-month rolling average.

$$E_{avg} = \frac{\sum_{i=1}^{12}(ER_i \times n_i)}{\sum_{i=1}^{12} n_i} \qquad (Eq. 10)$$

Where:

E_{avg}= Weighted 12-month rolling average Hg emission rate, (lb/MWh);

ER_i= Monthly Hg emission rate, for month "i", (lb/MWh); and

n = Number of unit operating hours in month "i" with valid CEM and electrical output data, excluding hours of unit startup, shutdown, and malfunction.

(3) If a sorbent trap monitoring system is used in lieu of a Hg CEMS, as described in §75.15 of this chapter and in appendix K to part 75 of this chapter, calculate the monthly Hg emission rates using Equations 7 through 9 of this section, except that for a particular pair of sorbent traps, $C_h$in Equation 7 shall be the flow-proportional average Hg concentration measured over the data collection period.

(i) Daily calibration drift (CD) tests and quarterly accuracy determinations shall be performed for Hg CEMS in accordance with Procedure 1 of appendix F to this part. For the CD assessments, you may use either elemental mercury or mercuric chloride (Hg° $HgCl_2$) standards. The four quarterly accuracy determinations shall consist of one RATA and three measurement error (ME) tests using $HgCl_2$standards, as described in section 8.3 of Performance Specification 12–A in appendix B to this part (note: Hg° standards may be used if the Hg monitor does not have a converter). Alternatively, the owner or operator may implement the applicable daily, weekly, quarterly, and annual quality assurance (QA) requirements for Hg CEMS in appendix B to part 75 of this chapter, in lieu of the QA procedures in appendices B and F to this part. Annual RATA of sorbent trap monitoring systems shall be performed in accordance with appendices A and B to part 75 of this chapter, and all other quality assurance requirements specified in appendix K to part 75 of this chapter shall be met for sorbent trap monitoring systems.

§ 60.51Da Reporting requirements.

(a) For SO_2, NO_X, PM, and Hg emissions, the performance test data from the initial and subsequent performance test and from the performance evaluation of the continuous monitors (including the transmissometer) are submitted to the Administrator.

(b) For $SO_2$and $NO_X$the following information is reported to the Administrator for each 24-hour period.

(1) Calendar date.

(2) The average $SO_2$and NO_Xemission rates (ng/J or lb/MMBtu) for each 30 successive boiler operating days, ending with the last 30-day period in the quarter; reasons for non-compliance with the emission standards; and, description of corrective actions taken.

(3) Percent reduction of the potential combustion concentration of $SO_2$for each 30 successive boiler operating days, ending with the last 30-day period in the quarter; reasons for non-compliance with the standard; and, description of corrective actions taken.

(4) Identification of the boiler operating days for which pollutant or diluent data have not been obtained by an approved method for at least 75 percent of the hours of operation of the facility; justification for not obtaining sufficient data; and description of corrective actions taken.

(5) Identification of the times when emissions data have been excluded from the calculation of average emission rates because of startup, shutdown, malfunction (NO_Xonly), emergency conditions (SO_2only), or other reasons, and justification for excluding data for reasons other than startup, shutdown, malfunction, or emergency conditions.

(6) Identification of "F" factor used for calculations, method of determination, and type of fuel combusted.

(7) Identification of times when hourly averages have been obtained based on manual sampling methods.

(8) Identification of the times when the pollutant concentration exceeded full span of the CEMS.

(9) Description of any modifications to CEMS which could affect the ability of the CEMS to comply with Performance Specifications 2 or 3.

(c) If the minimum quantity of emission data as required by §60.49Da is not obtained for any 30 successive boiler operating days, the following information obtained under the requirements of §60.48Da(h) is reported to the Administrator for that 30-day period:

(1) The number of hourly averages available for outlet emission rates (no) and inlet emission rates (n_i) as applicable.

(2) The standard deviation of hourly averages for outlet emission rates (s_o) and inlet emission rates (s_i) as applicable.

(3) The lower confidence limit for the mean outlet emission rate (E_o*) and the upper confidence limit for the mean inlet emission rate (E_i*) as applicable.

(4) The applicable potential combustion concentration.

(5) The ratio of the upper confidence limit for the mean outlet emission rate (E_o*) and the allowable emission rate (E_{std}) as applicable.

(d) If any standards under §60.43Da are exceeded during emergency conditions because of control system malfunction, the owner or operator of the affected facility shall submit a signed statement:

(1) Indicating if emergency conditions existed and requirements under §60.48Da(d) were met during each period, and

(2) Listing the following information:

(i) Time periods the emergency condition existed;

(ii) Electrical output and demand on the owner or operator's electric utility system and the affected facility;

(iii) Amount of power purchased from interconnected neighboring utility companies during the emergency period;

(iv) Percent reduction in emissions achieved;

(v) Atmospheric emission rate (ng/J) of the pollutant discharged; and

(vi) Actions taken to correct control system malfunction.

(e) If fuel pretreatment credit toward the SO_2emission standard under §60.43Da is claimed, the owner or operator of the affected facility shall submit a signed statement:

(1) Indicating what percentage cleaning credit was taken for the calendar quarter, and whether the credit was determined in accordance with the provisions of §60.50Da and Method 19 of appendix A of this part; and

(2) Listing the quantity, heat content, and date each pretreated fuel shipment was received during the previous quarter; the name and location of the fuel pretreatment facility; and the total quantity and total heat content of all fuels received at the affected facility during the previous quarter.

(f) For any periods for which opacity, SO_2or NO_Xemissions data are not available, the owner or operator of the affected facility shall submit a signed statement indicating if any changes were made in operation of the emission control system during the period of data unavailability. Operations of the control system and affected facility during periods of data unavailability are to be compared with operation of the control system and affected facility before and following the period of data unavailability.

(g) For Hg, the following information shall be reported to the Administrator:

(1) Company name and address;

(2) Date of report and beginning and ending dates of the reporting period;

(3) The applicable Hg emission limit (lb/MWh); and

(4) For each month in the reporting period:

(i) The number of unit operating hours;

(ii) The number of unit operating hours with valid data for Hg concentration, stack gas flow rate, moisture (if required), and electrical output;

(iii) The monthly Hg emission rate (lb/MWh);

(iv) The number of hours of valid data excluded from the calculation of the monthly Hg emission rate, due to unit startup, shutdown and malfunction; and

(v) The 12-month rolling average Hg emission rate (lb/MWh); and

(5) The data assessment report (DAR) required by appendix F to this part, or an equivalent summary of QA test results if the QA of part 75 of this chapter are implemented.

(h) The owner or operator of the affected facility shall submit a signed statement indicating whether:

(1) The required CEMS calibration, span, and drift checks or other periodic audits have or have not been performed as specified.

(2) The data used to show compliance was or was not obtained in accordance with approved methods and procedures of this part and is representative of plant performance.

(3) The minimum data requirements have or have not been met; or, the minimum data requirements have not been met for errors that were unavoidable.

(4) Compliance with the standards has or has not been achieved during the reporting period.

(i) For the purposes of the reports required under §60.7, periods of excess emissions are defined as all 6-minute periods during which the average opacity exceeds the applicable opacity standards under §60.42Da(b). Opacity levels in excess of the applicable opacity standard and the date of such excesses are to be submitted to the Administrator each calendar quarter.

(j) The owner or operator of an affected facility shall submit the written reports required under this section and subpart A to the Administrator semiannually for each six-month period. All semiannual reports shall be postmarked by the 30th day following the end of each six-month period.

(k) The owner or operator of an affected facility may submit electronic quarterly reports for $SO_2$and/or $NO_X$and/or opacity and/or Hg in lieu of submitting the written reports required under paragraphs (b), (g), and (i) of this section. The format of each quarterly electronic report shall be coordinated with the permitting authority. The electronic report(s) shall be submitted no later than 30 days after the end of the calendar quarter and shall be accompanied by a certification statement from the owner or operator, indicating whether compliance with the applicable emission standards and minimum data requirements of this subpart was achieved during the reporting period. Before submitting reports in the electronic format, the owner or operator shall coordinate with the permitting authority to obtain their agreement to submit reports in this alternative format.

§ 60.52Da Recordkeeping requirements.

The owner or operator of an affected facility subject to the emissions limitations in §60.45Da shall provide notifications in accordance with §60.7(a) and shall maintain records of all information needed to demonstrate compliance including performance tests, monitoring data, fuel analyses, and calculations, consistent with the requirements of §60.7(f).

AIR QUALITY

SECOND EDITION

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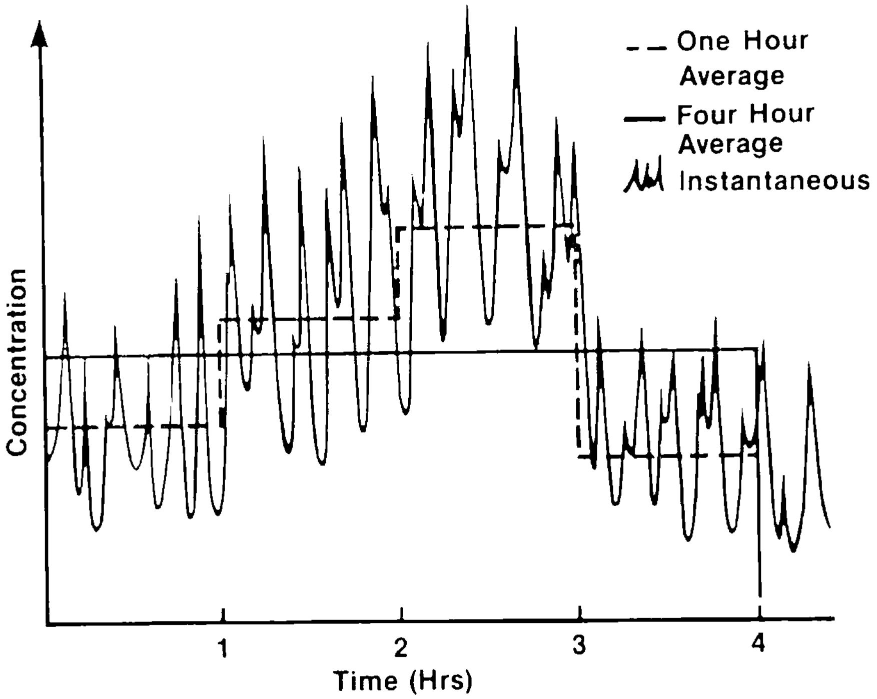

Figure 7.1 Averaging times for gaseous pollutants

Sampling Techniques

The principal objective of sampling is to collect a contaminant or contaminants for subsequent analysis and/or provide an environment for real-time measurements. Both require a system whereby gases or particles are drawn to the surface of a collecting medium or a sensing environment. These functions are accomplished by sampling trains which may include a vacuum pump, vacuum trap, a flow regulator and a collecting device or sensing unit. A bubbler type gas sampling train used to collect samples on an intermittent basis is illustrated in Figure 7.2. Sampling trains for gases may also utilize filters to prevent particles from entering the collection unit.

Based on the type of information desired and collection and analytical limitations, sampling may be conducted by static, grab, intermittent or continuous procedures. Such sampling procedures provide air quality data representing a range of averaging times, from the instantaneity of continuous systems to the 30-day average employed for some static samplers.

Static or passive sampling may involve the collection of contaminants by the diffusion of gases to a collection medium, the sedimentation of heavy

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David C. Foerter, ***Executive Director***
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Chad S. Whiteman, ***Deputy Director***
Email: cwhiteman@icac.com

June 29, 2004

Honorable Michael Leavitt, Administrator
U.S. Environmental Protection Agency
EPA Docket Center (Air Docket)
Mail Code: 6102T, Room B-108
1200 Pennsylvania Avenue, NW
Washington, DC 20460

Attention Docket ID No. OAR-2002-0056

Dear Administrator Leavitt:

The Institute of Clean Air Companies (ICAC) is the national trade association of companies that supply air pollution control and monitoring technology. Our members include nearly eighty leading suppliers of air pollution control and monitoring technologies for stationary sources. These companies operate and provide environmental solutions for affected industries as well as employment opportunities across the U.S.

The Institute congratulates EPA's efforts to propose a much-needed rule that provides for the reduction of mercury emissions from coal- and oil-fired electric generating facilities in order to protect public health. The Institute has a few observations concerning the proposed Utility Mercury Reduction Rule specifically concerning the performance of control technologies, technology guarantees, commercial availability, control costs, by-product disposal, and availability of construction resources. The Institute has submitted two separate sets of comments addressing mercury control and measurement technologies.

The Institute recommends that EPA pursue a regulatory framework that fully encompasses the capability and capacity of the air pollution control and measurement industry to achieve substantial reductions in mercury emissions, and then, provide regulatory flexibility to enable the most cost effective application of a range of technologies. Based on our thorough understanding of technology capabilities and the capacity of our industry to supply these technologies, we believe that a 50 to 70 percent reduction in current mercury emissions is feasible by 2008 to 2010. As a result, emissions would be reduced to a maximum of 14 to 24 tons. We note that compliance flexibility would enable a cap based on a 70 percent reduction, with some units able to achieve reductions of 90 percent and greater, and some units as low as 50 percent. Setting an appropriately stringent cap and then providing compliance flexibility would moderate any performance differences at individual units due to differences in coal, equipment, and flue gas characteristics. However, giving priority to compliance flexibility over the adequate consideration of a feasible emission cap, such as occurred in this proposed rule, fails to address the public health issues.

The attached ICAC comments provide both general and detailed comment that support the development of a mercury control rule with greater benefits.

We look forward to working with EPA on this important issue and invite you and your staff to contact me if you have any questions.

Sincerely,

David C. Foerter
Executive Director, ICAC

Enclosure a/s

GENERAL COMMENT

The rapid development of mercury control technologies over the last several years has produced a number of technologies that are available for the implementation of a national mercury control regulation for coal- and oil-fired power plants. A large number of laboratory tests and full-scale demonstrations have been conducted that provide information on the effectiveness of controls for various coal types and control configurations. Despite the current lack of a national control requirement for mercury, a number of options are commercially available while others are still in the development and testing phases.

Past experience with technology development for other pollutants (SO_2, NO_x, and PM) as well as other source categories such as mobile sources, suggests that delaying the regulation of mercury emissions from power plants would serve to delay the development of innovative control technologies. Research and development efforts are unlikely to be sustained at a vigorous level in the absence of regulatory or other drivers capable of creating a viable market for advanced control technologies. Larger markets provide more incentives for the development of technologies as well as foster competition between vendors that produces more innovative and cost effective solutions for affected sources. Smaller markets such as those that may be developed with the implementation of State regulations (e.g. Massachusetts, Connecticut, Wisconsin, New Jersey, North Carolina) are beneficial to the air pollution control industry but will be less effective in developing healthy markets than a timely implemented national program.

With the implementation of a national program, multiple control options including precombustion, combustion and post combustion technologies will contribute to meeting the required emission reductions. Coal cleaning as well as coal switching are examples of options that have the potential to reduce mercury emissions prior to fuel combustion.

Based on the recent test results, significant amounts of mercury can be removed through the use of existing controls. Existing control installations such as fabric filters, electrostatic precipitators, SO_2 scrubbers, and selective catalytic reduction (SCR) are currently achieving an estimated 36% reduction in mercury emissions even though these processes were not originally designed nor optimized for mercury capture. This is based on EPA's information collection request findings that an estimated 75 tons of mercury was contained in coal burned by power plants while 48 tons were emitted out of the stack. The current level of co-benefit control varies significantly with some combinations of control devices and coal types achieving as much as 90% removal and others not demonstrating any co-benefit control. With the implementation of mercury regulation beyond incidental co-benefit levels of control, a number of options for optimization of existing controls will be implemented to provide cost effective reductions in a short period of time.

Mercury specific control technologies such as sorbent injection systems have been demonstrated at full-scale. Multipollutant control approaches as well as other mercury specific technologies have also demonstrated significant progress and will provide additional low cost, innovative approaches to mercury control. A number of these technologies, including sorbent injection systems as well as SCR coupled with wet FGD, have achieved removal rates greater than 90% under certain circumstances.

Under the Section 112 MACT proposal, EPA also made projections for mercury control installations. These projections were based on the assumption that the Clean Air Interstate Rule/Interstate Air Quality Rule (CAIR/IAQR) would not be implemented and the co-benefit control from SO_2 and NO_x control installations would not be realized. Based on the development and enhancement of mercury removal from existing controls, significant reductions in mercury emissions are likely to occur without touching the potential of currently available control technologies. Also under the Section 112 MACT proposal, EPA did not consider ACI technology in the development of the MACT floor as EPA stated that this technology was not demonstrated nor commercially available (U.S. EPA, 2004). Activated carbon injection is commercially available and has been demonstrated on at least four full-sized coal-fired plants to-date with additional full-sized tests scheduled later this year (see details below). Outside of the United States, the Berrenrath 275 MW and the Wachtberg 166 MW plants in Germany operate on carbon injection technology to control mercury. Based on this knowledge, EPA should consider ACI in the development of the MACT floor as it is a viable technology for the electric power sector that has also been proven in other industrial sectors to control mercury emissions. What is contradictory in EPA's analysis is that they used ACI in their cost modeling exercises with the integrated planning model (IPM) but failed to recognize this technology in setting the level of mercury reductions for the MACT requirement.

Based on the current availability of mercury specific control options and the near term development of other promising technologies, EPA's own analysis (ref: Office of Research and Development submittal to the e-docket) has indicated that a reduction of 50-70% of current emission levels in the 2008 to 2010 timeframe is justifiable. This corresponds to annual mercury emissions of between 14-24 tons for the electric power sector. This level of reduction seems even more reasonable considering that EPA estimated that the co-benefit level of mercury emissions cap under the 2003 Clear Skies proposal was initially set at a first phase level of 26 tons of mercury emissions in 2010. The first phase cap is somewhat below EPA's estimated co-benefits estimate of 30 tons, and switching by units to different coal types with lower mercury content would be likely for compliance with mercury control requirements. The current mercury control proposal made under the Clean Air Act, Section 111 provisions would not create markets for technology development nor encourage innovation as the projected mercury cap level was set at the revised co-benefit level that is much higher at 34 tons. Additionally, EPA's modeling analysis does not consider the low cost reductions that will come from enhancing existing control technologies for greater mercury capture. These innovations will reduce the cost and overall demand for mercury specific reductions. EPA's projections for mercury specific control installations under the Section 111 proposal estimate that only 1 GW, or approximately two of the more than 1000 coal-fired boilers in the U.S., would install mercury control technologies by 2010.

Concerning the regulatory mechanism used for a mercury control program, ICAC would recommend including flexible mechanisms in the regulation that would encourage innovation while providing a clear goal with meaningful reductions. Examples of these types of mechanisms include early reduction incentives, market based approaches, capital recovery programs, plant wide averaging, safety valves or other approaches. These types of incentives combined with concrete goals would encourage technology innovation and reduce impacts on generation mix.

The air pollution control industry already has considerable experience with the implementation of mercury controls for other industrial sectors. Sorbent injection has been commercially proven to augment the removal of mercury in waste-to-energy plants. Experience controlling mercury emissions has been gained in more than 60 US and 120 international waste-to-energy plants which burn municipal or industrial waste or sewage sludge. For the past two decades, sorbent injection upstream of a baghouse has been successfully used for removing mercury from flue gases from these facilities. Other reagents used include activated carbon, lignite coke, sulfur containing chemicals, or combinations of these compounds. The mercury control experience gained from the municipal and industrial waste combustors demonstrates that the air pollution control industry has been able to control mercury in the past and is able to apply their expertise to the electric power sector.

TECHNOLOGIES AND PERFORMANCE

The list of technologies provided below is not intended to be an exhaustive list of the available mercury control technologies as there are many new and emerging technologies not listed. The technologies below are just a sample of the technologies that are currently available or under development but will be available soon.

Sorbent Injection Systems

Injecting a sorbent such as powdered activated carbon, bromine, poly sulfides, or other sorbent into the flue gas represents a relatively simple approach to controlling mercury emissions from coal-fired boilers. The gas-phase mercury in the flue gas contacts the sorbent and attaches to its surface. The sorbent with the mercury attached is then collected by the existing particle control device, either an electrostatic precipitator (ESP) or fabric filter (FF) as shown in Figure 1. This combined material, consisting of 99% fly ash and 1% sorbent, is then either disposed of or beneficially used.

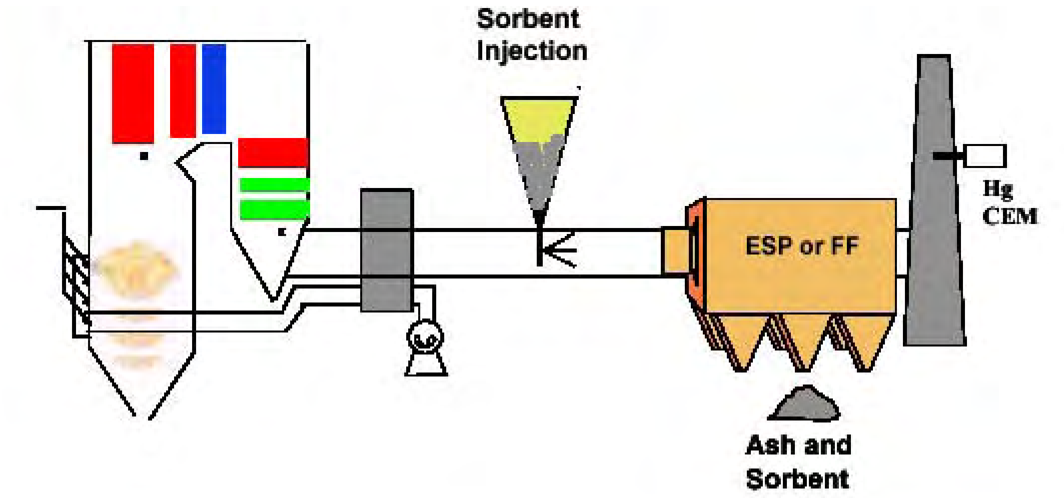

Figure 1. Schematic Diagram of Sorbent Injection Process

The type of particulate control equipment installed at the plant is a key parameter defining both the amount of sorbent that is required and the ultimate limitation of the amount of mercury that can be removed. The two primary particulate control devices are ESPs and fabric filters. When the sorbent is injected into the flue gas it mixes with the gas and flows downstream. This provides an opportunity for the mercury in the gas to contact the sorbent and be removed. This is called "in flight" capture. The sorbent is then collected in the particulate control device where there is a second opportunity for sorbent to contact the mercury in the gas. Because a fabric filter provides better contact than an ESP between the sorbent and the vapor-phase mercury, higher levels of mercury removal can be achieved at lower sorbent rates on units with a fabric filter. Currently only 10% of the power plants have fabric filters and the other 90% have ESPs.

Four full-scale demonstrations were conducted during 2001 and 2002 under a cooperative agreement from the Department of Energy National Energy Technology Laboratory (DOE/NETL), ADA-ES, PG&E National Energy Group (NEG), We

Energies, Alabama Power Company, Ontario Power, TVA, FirstEnergy, and EPRI. Follow-on funding was received for additional tests being conducted in 2003.

The first program was completed in the spring of 2001 at the Alabama Power E.C. Gaston Station (Bustard et al., 2002). This unit burns a low-sulfur bituminous coal and uses a hot-side ESP followed by a COHPAC™ fabric filter as a secondary collector for remaining fly ash. Activated carbon was injected into the fabric filter. The second program was conducted during the fall of 2001 at the WEC Pleasant Prairie Power Plant (PPPP) (Starns et al., 2002). This unit burns a subbituminous Powder River Basin (PRB) coal and uses an ESP to collect the carbon and fly ash. The third program was completed in the summer of 2002 at PG&E National Energy Group's Brayton Point Station (Durham et al., 2002). This unit burns low-sulfur bituminous coals and uses ESPs for particulate control. The fourth program was completed in the fall of 2002 at PG&E National Energy Group's Salem Harbor Station. Salem Harbor fires bituminous coals with an ESP for particulate control and an SNCR system for NO_x control.

Figure 2 presents full-scale data from two sites with ESPs; one bituminous coal and the other a Powder River Basin (PRB) coal. For both cases, mercury removal increases with increased rates of carbon injection. For the PRB coal, mercury removal was limited to 70% across the ESP. This limitation is most likely due to the trace amounts (< 1 ppm) of HCl available in the gas stream. For the bituminous coal, mercury removal exceeded 90% at the highest carbon injection rate. This coal has a high chloride content that resulted in approximately 150 ppm of HCl.

Manual mercury measurements were made at all sites following the draft Ontario Hydro method. Table 1 presents measurement results from the PRB test site with carbon injected upstream of an ESP. These tests show that the overall removal was 73% even though the majority of the mercury was in the elemental form, which is thought to be the more difficult form to capture. In fact, the collection efficiency was nearly identical for both elemental and oxidized mercury. This test is typical of all of the results that validate the capability of powdered activated carbon to capture all forms of mercury from both bituminous and subbituminous coals.

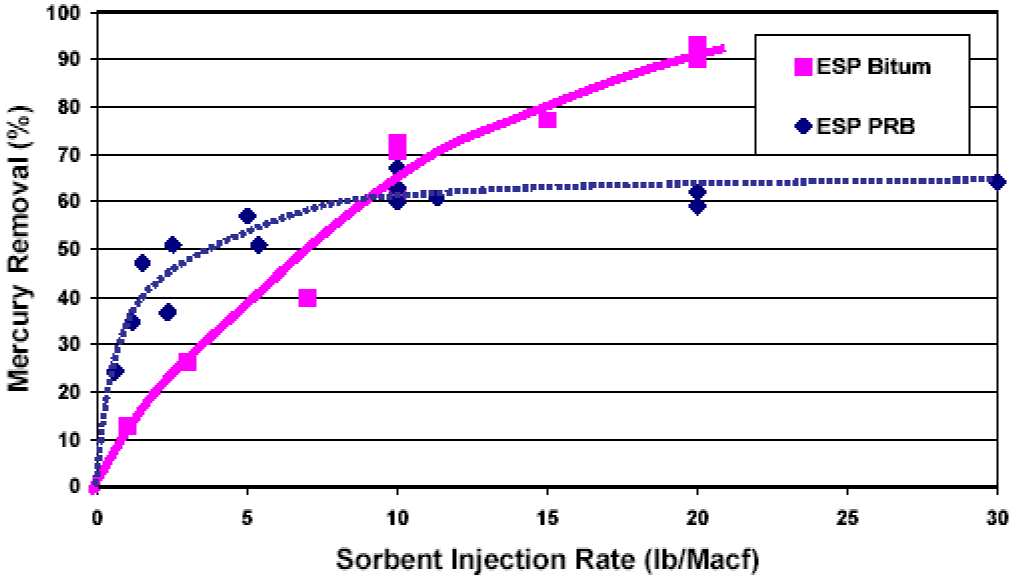

Figure 2. Mercury Removal with Activated Carbon Injection Upstream of an ESP

Table 1. Speciated Mercury Measured by the Ontario Hydro method, long-term tests with activated carbon injection concentration = 11 lbs/MMacf. Tests conducted at Pleasant Prairie Power Plant in fall 2001 (note: The configuration used at this facility made the ash unsuitable for sale).

	Particulate (µg/dncm)	Elemental (µg/dncm)	Oxidized (µg/dncm)	Total (µg/dncm)
ESP Inlet	1.0	14.7	1.7	17.4
ESP Outlet	0	4.3	0.4	4.7
Removal Efficiency (%)	100	70.7	74.5	72.9

Figure 3 shows performance of activated carbon injection (ACI) upstream of a fabric filter. This plot includes full-scale data from Plant Gaston on a bituminous, and reduced-scale tests conducted by EPRI on a PRB coal (Sjostrom, 2002a). The data from both fabric filter test programs show that ACI can produce 90% removal of mercury for both bituminous and subbituminous coals. Comparing the data from the fabric filter results in Figure 3 with the ESP results in Figure 2, it can be seen that the increased contact between the flue gas and the sorbent in the dust cake reduces the carbon feed requirements by nearly a factor of ten.

Ontario Hydro measurements of mercury removal during ACI tests with a fabric filter at Plant Gaston are presented in Table 2. As can be seen, the activated carbon is effective for both species of vapor-phase mercury.

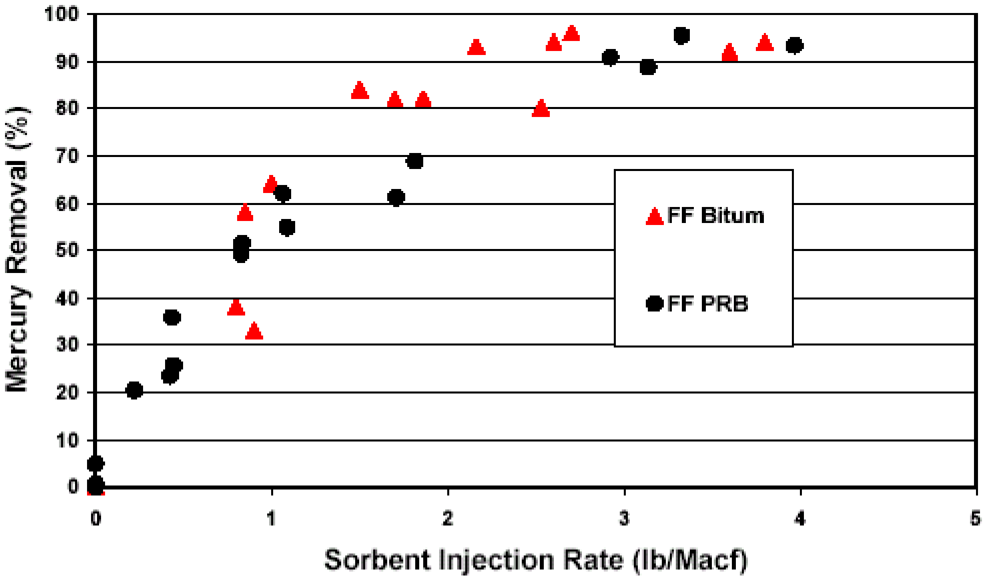

Figure 3. Mercury Removal with Activated Carbon Injection Upstream of a Fabric Filter.

Table 2. Average Mercury Removal Efficiencies Across COHPAC™ as Measured with the Ontario Hydro method.

Sampling Location	Particulate (µg/dncm[1])	Oxidized (µg/dncm[1])	Elemental (µg/dncm[1])	Total (µg/dncm[1])
COHPAC Inlet	0.2	6.4	4.6	11.2
COHPAC Outlet	0.1	0.9	0.0	1.1
Removal Efficiency (%)	50	86	99	90

Long-Term TOXECON Field Test at E. C. Gaston Station

The results of the first field test program at Gaston provided a good indication of the capabilities and limitations of the TOXECON technology for controlling mercury. However, the tests were performed for a limited amount of time, less than 200 hours of continuous operation, and did not allow for a thorough operational analysis of the use of this technology for mercury control. In the fall of 2002, ADA-ES was selected by the DOE to continue to mature the technology and conduct a long-term test program at the Gaston Station.

This program provides the first opportunity to evaluate activated carbon in the TOXECON configuration for a year of operation. Although new TOXECON units may be designed more conservatively than COHPAC units, important long-term operating data will be obtained through this test. Technical and financial support on this program will be provided by Southern Company and Alabama Power, the EPRI, Allegheny Energy, Arch Coal, Inc., FirstEnergy, Hamon Research-Cottrell, Ontario Power Generation, Duke Power and TVA (Durham, et al., 2003).

Figure 4 shows a plot of inlet and outlet mercury concentrations and overall mercury removal during four months of continuous operation. As can be seen, in spite of significant variability in the inlet mercury, the system has been able to maintain consistent levels of mercury removal with an overall average above 85%. These results further demonstrate the effectiveness of activated carbon injection for reducing mercury emissions. This technology is ideally suited for use on existing coal-fired boilers as it provides the following advantages: minimal capital cost of equipment (<$3/kW); can be retrofit with little or no downtime of the operating unit; effective for both bituminous and subbituminous coals; and can achieve 90% removal when used with a fabric filter that has been designed properly for carbon injection.

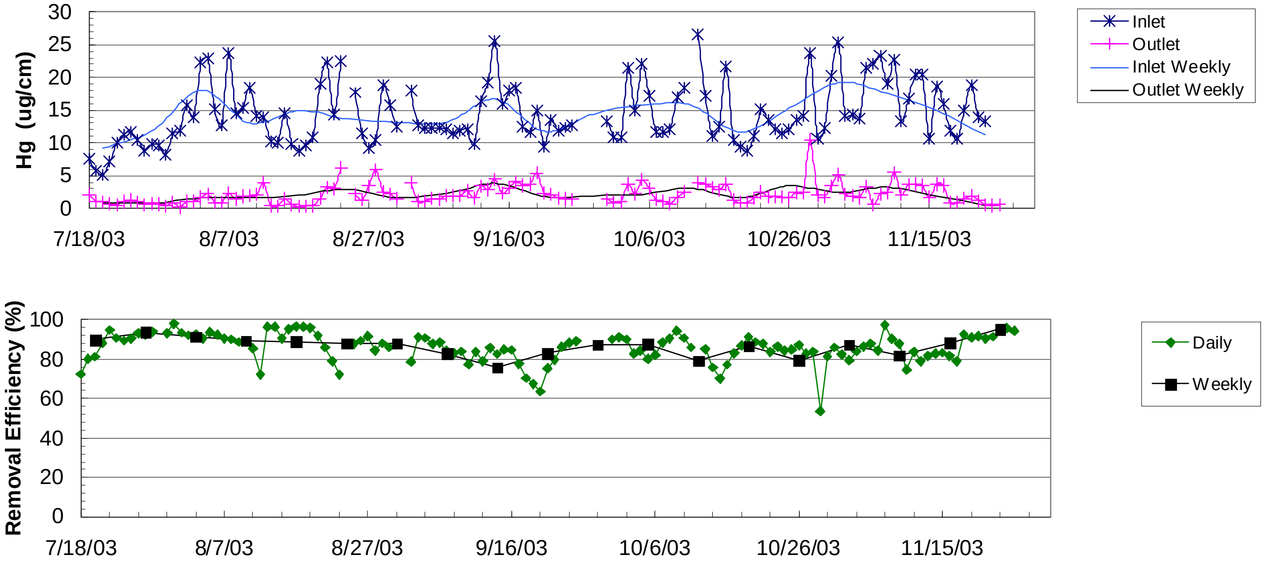

Figure 4. Inlet and Outlet Mercury Concentrations and Removal Efficiency for Toxecon Technology During Four Months of Operation at E. C. Gaston Station

Multipollutant Control Approaches

In anticipation of markets fostered by regulation or legislation, a number of multi-pollutant control technologies that also reduce mercury are currently being demonstrated. The long-term viability of these technologies for the coal-fired power market largely depends on meaningful regulation to enable a commercial market in which these technologies would compete. That competition among a range of technologies, and enabled with flexibility within regulation, leads to the availability of increasingly cost-effective control options. Information has been included on electro-catalytic oxidation and a pre-combustion control technologies, technologies with vastly different approaches on how to address the same multi-pollutant problem on coal-fired power units.

Electro-Catalytic Oxidation (ECO) is an integrated multi-pollutant control technology that achieves major reductions in emissions of NO_x, SO_2 , fine particulate matter, and mercury from the flue gas of coal-fired power plants. The process also produces a valuable fertilizer co-product that reduces operating costs and avoids landfill disposal of waste.

ECO treats flue gas in three steps to achieve multi-pollutant removal as shown in Figure 5. In the first step of the process, a barrier discharge reactor oxidizes gaseous pollutants to higher oxides. For example, nitric oxide is oxidized to nitrogen dioxide and nitric acid, a small portion of the sulfur dioxide is converted to sulfuric acid, and mercury is oxidized to mercuric oxide. Following the barrier discharge reactor is an ammonia scrubber that removes the sulfur dioxide and the oxides of nitrogen. A wet electrostatic precipitator (WESP) follows the scrubber that in combination captures acid aerosols produced by the discharge reactor, fine particulate matter and oxidized mercury.

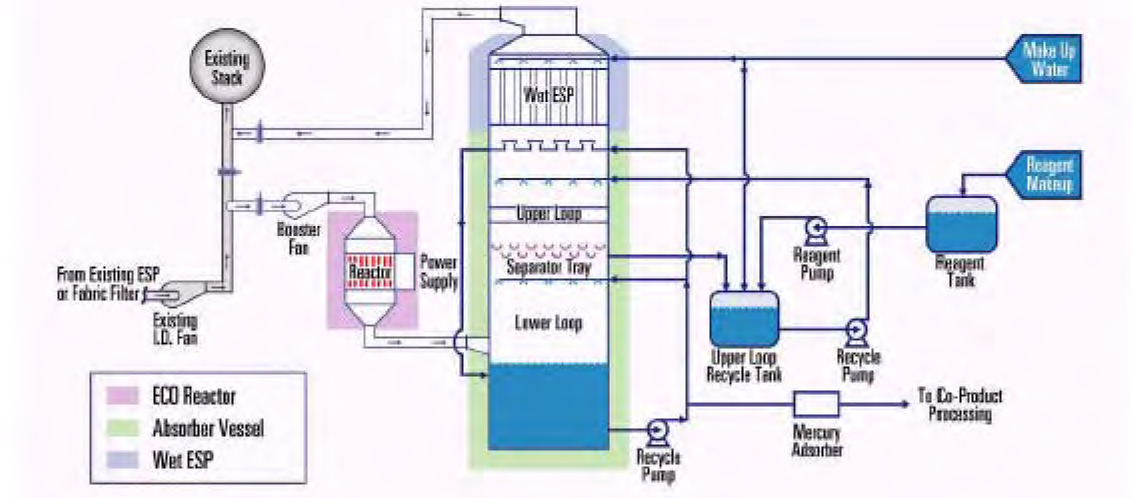
Existing Stack
Wet ESP
Make Up Water
Reagent Makeup
Upper Loop
Booster Fan
Reactor
Power Supply
Separator Tray
Reagent Pump
Reagent Tank
From Existing ESP or Fabric Filter
Existing I.D. Fan
Lower Loop
Upper Loop Recycle Tank
Recycle Pump
To Co-Product Processing
ECO Reactor
Absorber Vessel
Wet ESP
Mercury Adsorber
Recycle Pump

Figure 5. Schematic Diagram of Electro-Catalytic Oxidation (ECO) Process

The ECO process has undergone pilot scale testing on a 1-2 MW flue gas slipstream at FirstEnergy's R.E. Burger Plant for 2 years. In addition, a 50 MW commercial demonstration has been constructed at the same plant. The R.E.

Burger Plant burns a blend of eastern bituminous and western sub-bituminous coals with oxidized mercury being the predominant mercury species measured. The pilot testing has been successful and has shown that the ECO process consistently achieves 80 to 90% capture of the mercury contained in the plant's exhaust gas. Due to the multi-pollutant nature of this technology, the ECO pilot was also able to achieve greater than 90% NO_x removal, 98% SO_2 removal, and 96% removal of particles under 3 microns in size. A mercury semi-continuous emission monitoring system was recently installed on the 50 MW commercial demonstration unit. Although data is not yet available, total mercury removal is projected to be 80 to 90%; consistent with results obtained during pilot testing.

Pre-combustion coal scrubbing process was developed at Stanford Research Institute and currently holds the U.S. patent as *K-Fuel*. Pre-combustion cleaning of pollutants and their precursors is another mechanism to address multi-pollutant control issues on coal-fired power facilities, particularly the low rank coals such as lignite and western sub-bituminous coals. The established pre-combustion technology uses heat and pressure to physically and chemically transform low Btu, high moisture content low-rank coals, such as western sub-bituminous coal and lignite, into a high Btu, low moisture fuel. This coal processing technology increases energy efficiency of sub-bituminous coal and lignite by 30-55%. An added benefit of this technology is that 65-70% of mercury is removed, with as high as 90% reduction in some cases, and up to 30% of SO_2 and NO_x removed from the initial feedstock. During the process of removing the water, mercury is volatized and released in the gas and water off-streams. The mercury and other pollutants are captured with carbon filters and disposed of at permitted disposal sites. The result is a pollutant scrubbed high energy coal. The number and geographic scope of patents around the world that are applicable to this technology have increased dramatically in anticipation to requirements for a wide range of coal types.

As demonstrated in Table 3, the resultant coal product improves the quality of low-grade western and lignite coals, increasing efficiency of steam generating units, and offering another approach for facilities to comply with air emissions standards. Since western sub-bituminous coal is typically already low in mercury and sulfur before refining, facilities can substitute the scrubbed coal for bituminous coal feedstocks for significant emission reduction benefits.

Table 3. Product ComparisonBetween Sub-bituminous and Lignite, K-Fuel, and Eastern Coal

	Sub-bituminous and Lignite Coal[1]	K-Fuel™ Product	Eastern Compliance Bituminous Coal[2]
Heating Value (Btu/lb)	6,850-8,804	10,637-11,683	13,210
Moisture Content (%)	26.29-45	5.74-8.0	7
Mercury (ppm)	0.0289-0.342	0.008-0.163	0.15

Source: K-Fuel test data

[1] Includes four sub-bituminous and one lignite coal feedstock used in K-Fuel tests
[2] Average of Eastern Compliance Coal, USGS

The pre-combustion process employs both mechanical and thermal means to increase the quality of sub-bituminous coal and lignite by removing moisture, sulfur, nitrogen, mercury, and other heavy metals. Because these constituents are removed before burning the coal at the plant, this form of control can virtually replace the need for post-combustion controls.

The K-Fuel process diagram is given in Figure 6 below. To start the process, raw coal is delivered directly from a mine to the coal processing facility. The coal enters the first stage separator, developed using conventional coal cleaning technology, where it is crushed and screened to remove the large rock and rock material. The processed coal is then transferred to an intermediate storage facility prior to being sent via a distribution system to the specialized thermal process. This process essentially operates like a giant pressure cooker, utilizing Lurgi Mark IV vessels under high pressure and temperature to place thermal stress on the coal. The coal passes through pressure locks into the processors, and then steam is injected into the processors at 460° F and 485 psi. The coal is maintained at these conditions, and the mineral inclusions are fractured under the thermal stress, removing both the included rock (containing some mercury) and sulfur-forming pyrites. The inherent moisture of the coal also released.

After being treated for a sufficient time in the main processor, the coal is discharged into a second pressurized lock, which is sealed off from the primary reactor. After sealing, the processor pressure is vented into a water condenser to return the processor to atmospheric pressure, and to flash cool the coal to approximately 200°F. The coal is then discharged onto a belt and further cooled by convection and indirect cooling. Following cooling, the coal is sent to a second stage separator for additional screening to remove sulfur- and mercury-containing material liberated by the thermal process. Water liberated from the coal is removed at various points in the process. This water, along with some condensed process steam, is either sent directly to treatment or is reused within the process. The water treatment system removes coal fines and hydrocarbon compounds liberated from the coal in the processor, and uses carbon filtering to remove mercury and other heavy metals that were released from the coal and rock. The waste products (carbon, mercury, and heavy metals) from the filtering process are sent to a qualified, permitted disposal site for final disposition.

Third party and company tests have demonstrated the clean-burning qualities of the patented pre-combustion product. Results reported in 2002 indicated the ability to achieve 70% mercury removal when using Wyoming Wyodak sub-bituminous coal, and up to 65% mercury removal when using Louisiana Dolet Hills lignite coal.

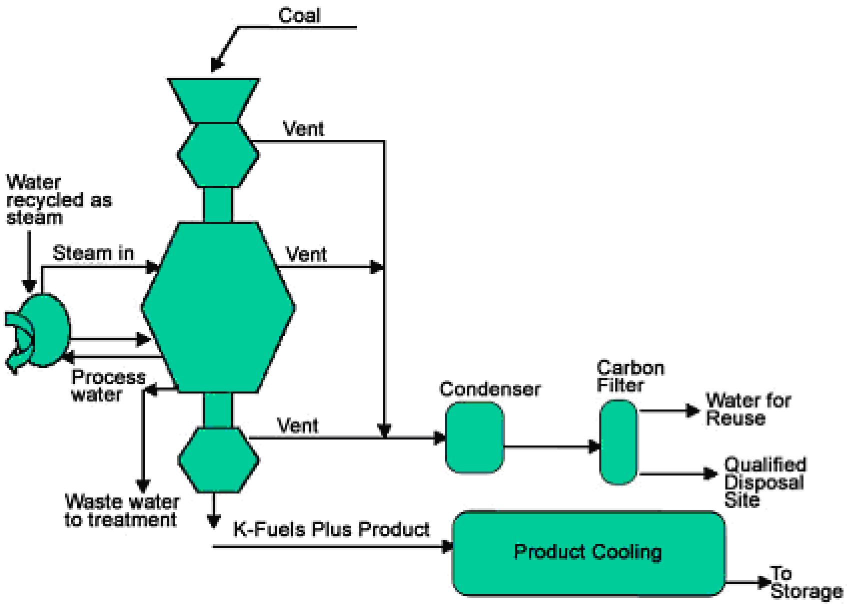
Coal
Vent
Water recycled as steam
Steam in
Vent
Process water
Condenser
Carbon Filter
Water for Reuse
Vent
Qualified Disposal Site
Waste water to treatment
K-Fuels Plus Product
Product Cooling
To Storage

Figure 6. K-Fuel Thermal Processing Plant

The first commercial 750,000 ton per year K-Fuel plant will be in operation by the end of the first quarter of 2005 near Gillette, Wyoming. In early May 2004, the company announced an agreement-in-principle to locate the first commercial K-Fuel plant at the Buckskin Mine, north of Gillette. The Buckskin mine has the potential to be expanded to 8 million tons per year of capacity. In addition, the company announced a signed agreement to purchase the Fort Union Mine site and related facilities.

The commercial plant currently under development is fully funded and approximately two-thirds of the production from the initial 750,000 tons per year plant has been committed, with the balance to be used for test burns to facilitate future contract commitments, for plant expansions, and future coal processing facilities. There are plans to own and operate coal processing production facilities, as well as license the technology to third parties. These coal processing facilities plants are built using proven, off-the-shelf, modular equipment designed by Lurgi SA, that allows for adding capacity to each plant as demand grows.

Enhancing Control Through Existing Control Technologies

Mercury may be removed from the flue gas of coal-fired boilers to a greater or lesser extent by devices such as electrostatic precipitators, baghouses, SCRs, and SO_2 scrubbers used to control other emissions. The efficiency of such co-beneficial collection depends on the specific equipment and operating parameters, as well as on the chemical form of mercury in the flue gas, which in turn is influenced by fuel composition and combustion parameters.

Sorbent addition in wet scrubbers has been shown to be highly effective in capturing the oxidized portion of mercury in the vapor phase in boiler flue gas. This is because vaporous mercury that is in an oxidized rather than elemental form is soluble. Scrubbers have been shown to be highly effective in capturing the oxidized mercury in the vapor phase in boiler flue gas, on the order of 60-80% depending on site specifics and fuel factors. Addition of sulfides is being used to retain the mercury in solution and prevent a small fraction of the captured mercury that can potentially be re-emitted as elemental mercury.

Wet FGD systems are currently installed on about 25 percent of the coal-fired utility generating capacity in the U.S., representing about 15 percent of the total number of coal-fired units. Depending on the effects of the operating parameters, FGD systems can provide a cost-effective, near-term mercury emissions control option with a proven history of commercial operation. For boilers already equipped with FGD systems, the incremental cost of any vapor-phase mercury removal achieved is minimal. To be widely accepted and implemented, technical approaches that improve mercury removal performance for wet FGD systems should also have low incremental costs and have little or no impact on operation and SO_2 removal performance.

Mercury Oxidation in Selective Catalytic Reduction System: The speciation of mercury is known to have a significant impact on the ability of air pollution control devices to capture mercury. The oxidized form of mercury is highly water soluble, therefore, it is easier to capture in wet FGD systems than the elemental form of mercury which is not water-soluble. The oxidized form of mercury is also more easily adsorbed than elemental mercury on unburned carbon in the flyash and on injected sorbents. SCR catalysts act to oxidize a significant portion of the elemental mercury, making it easier to remove it in downstream wet FGD systems or PM collection sevices.

SCRs are already used for reducing NO_x emissions on close to 100 GW of the approximately 310 GW of coal-fired capacity in the U.S. Additional SCR installations are projected to occur due to existing ozone-related rules including: NO_x SIP call, State Regulations and the proposed CAIR/IAQR. SCR catalyst is known to oxidize elemental mercury to oxidized mercury forms such as $HgCl_2$ that are more easily captured and removed by downstream air pollution control equipment (Lee et al., 2003). Mercury oxidation is enhanced by lower temperature, higher coal chlorine content, and increased residence time. Due to the low gas-phase chlorine in flue gases from low-rank coals (e.g. sub-bituminous coals such as PRB), the mercury oxidation level over SCR catalyst has been found not to be as high as it is for flue gases in bituminous-fired units.

A number of simple approaches can achieve more mercury emissions control in a shorter timeframe. Under the NO_x SIP call, a cap-and-trade program to reduce NO_x emissions from power plants in 19 northeastern states and the District of Columbia is being implemented starting in May 2004. The emission limits governing affected sources under the NO_x SIP call only apply during a five-month ozone season from May through September. Year-round operation of the SCRs at those units could achieve greater mercury co-benefits as soon as implemented. Additionally, if SCRs are run October to April without ammonia injection, the absence of ammonia would result in higher mercury oxidation levels and thus downstream capture for all coal types where downstream FGD or PM capture devices will be in place. It is expected that many SCR installations will go to year-round operation under the existing and proposed rules, but early implementation of this approach can provide quicker co-benefits without the addition of new equipment.

If SCRs are run October to April with ammonia injection, the co-benefit of mercury oxidation will likely not be as high as mercury oxidation is inhibited by ammonia. However, it would still contribute significant mercury emissions control co-benefits due to full-year operation versus ozone season where effective downstream capture equipment is in place such as wet FGD.

Another approach would be to add an extra layer of catalyst to the existing SCR installations. The extra layer would be effective for both NO_x and mercury oxidation. Mercury oxidation would be enhanced due to the lower ammonia concentration in the last layer. The additional benefits include both additional NO_x reduction, that would generate valuable NO_x credits to defray the cost of the catalyst or even generate a net benefit, as well as higher co-benefits for mercury emissions control. Most or maybe all SCR installations in the U.S. already have provision for one or more extra layers built into the ductwork so that no additional construction would be needed to implement this approach and would have the highest co-benefit mercury capture where wet FGD or other effective capture equipment is in place downstream of the SCR.

New technologies are being developed for mercury oxidation across an SCR that inject chloride prior to the catalyst. The enhanced mercury oxidation is due to improved thermodynamics at regular SCR operating temperatures due to higher flue gas chloride concentrations which otherwise limits the extent of Hg oxidation possible. At low chloride levels, thermodynamics limit the extent of Hg oxidation that is possible. The higher chloride concentration makes the reaction possible while the catalyst speeds it up. This new patented technology will be especially useful for low-rank coals and will be ready for implementation in a short time horizon. This technology should greatly enhance the mercury co-benefits for sub-bituminous and lignite installations that have or will have SCR installations for NO_x control and where effective downstream capture equipment is or will be in place. It is expected that chloride concentrations downstream of the SCR would be no higher than typical chloride flue gas levels seen in average bituminous-fired units, and that chloride injection would not be necessary for flue gases already having high chloride levels.

CAPITAL AND OPERATING COSTS

Levelized capital and operating costs are generally low for mercury control approaches compared to new full-scale installation costs for control of criteria pollutants such as NO_x and SO_2. This is true for mercury control through enhancements to existing equipment such as SCR and wet FGD, as well as for installation of new equipment for mercury specific control technologies such as sorbent injection. In addition, the costs for mercury specific controls will likely decrease over time as more is learned about current approaches and new ideas are tested as has been seen in prior experience curves for pollution control equipment.

The costs for activated carbon injection technology consists of capital equipment and operating costs. The capital costs to retrofit an existing facility will depend on site-specific issues. Generally, the uninstalled cost for the sorbent injection equipment for power plants generating 100 to 500 MW is in the range of $600,000 to $1,000,000. The primary operating cost and the largest cost element for the technology is the cost of the throwaway sorbent. Figure 6 shows a plot of the sorbent costs in mils/kWh for both bituminous and subbituminous coals. For a unit with an ESP, the cost of the sorbent would be approximately 1.2 – 1.5 mils/kWh to achieve 60 to 70% mercury removal for both types of coals. If a unit has a fabric filter, it is expected that up to 90% mercury removal can be achieved at a sorbent cost of between 0.3 - 0.4 mils/kWh.

One option that a plant might consider is to trade off capital costs for operating costs by installing a fabric filter to reduce sorbent requirements. The cost of a pulse jet fabric filter designed for the collection of the injected activated carbon would be $40 - $50/kW and would result in a factor of three reduction in sorbent costs while achieving up to 90% mercury removal. This is an example of the importance of a regulation that gives the utility flexibility in how to achieve mercury reduction at each site.

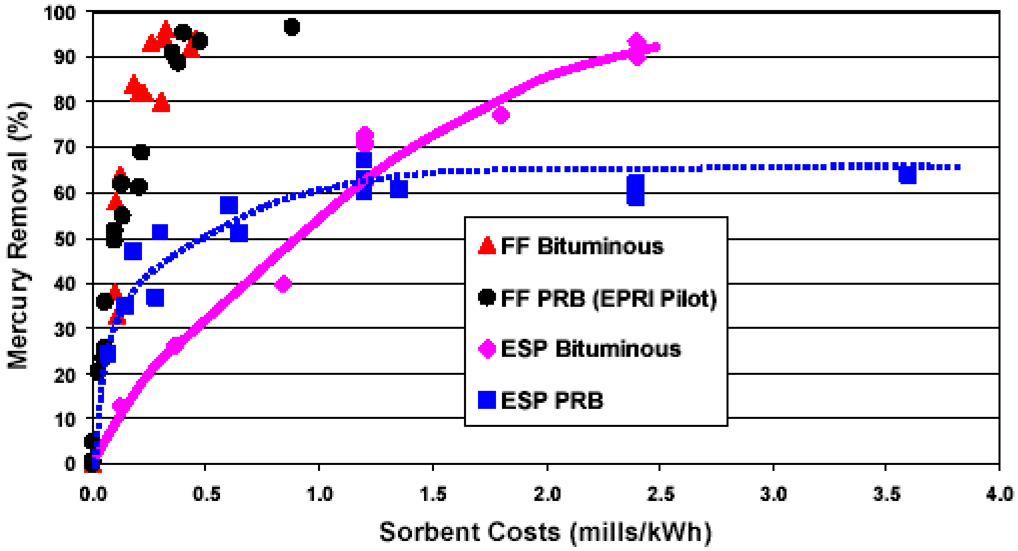

Figure 6. Costs of Sorbents for Mercury Control at Coal-Fired Power Plants.

As the ECO process is a multipollutant technology, the costs incorporate control of SO_2, NO_x, PM and mercury and are considerably higher. For the development of a compliance strategy for a particular unit, one must weigh the cost of control installations for individual pollutants such as scrubbers for SO_2, SCR or SNCR for NO_x, fabric filters for PM, etc. The capital cost associated with an ECO installation is estimated to be $200/kW, including balance of plant modifications. The operating costs are estimated to be 2.5 mils/kWh.

For the precombustion control option, the marketplace would ultimately establish the per ton price for clean, pre-combusted western sub-bituminous and lignite coal. K-Fuel would compete with eastern coal of a similar Btu heat value.

An analysis of the cost for the SCR mercury optimization options outlined above, as well as the new chloride injection technology is in progress and will be submitted to EPA shortly. The analysis looks only at the amount of electric generating capacity that is projected to be equipped with both SCR and wet FGD in the year 2010

SCR catalyst is already used for reducing NO_x emissions on about 100 GW of the approximately 300 GW of coal-fired capacity in the U.S. Currently, there is approximately 25 GW of coal-fired electric generating capacity in the U.S. equipped with both SCR and wet FGD. The amount of capacity equipped with both SCR and wet FGD is projected to rise to about 40 GW by 2005 and to about 93 GW by 2010 as companies install new control equipment to comply with NO_x requirements related to the NO_x SIP call and SO_2 and NO_x requirements related to the proposed Clean Air Interstate Rule. About 94 percent of the projected capacity equipped with both wet

FGD and SCR is expected to burn bituminous coal, with the remaining six percent burning sub-bituminous.

The in-progress analysis examines the mercury removal performance, associated costs of several optimization options, combinations of options for enhanced Hg oxidation, and capture for units that would be equipped with both SCR and wet FGD in the year 2010 with and without chloride injection technology.[1] *The analysis of the options for mercury control through SCR enhancements will be submitted to EPA shortly.*

Option 1—Operating SCRs Year-Round
Option 2—Installing an Additional Layer of SCR Catalyst
Option 3—Combination of Options 1 and 2, With Ammonia Injection
Option 4—Combination of Options 1 and 2, With No Ammonia Injection During the Non-Ozone Season (October 1-April 30)
Option 5--Chloride Injection

CONTROL TECHNOLOGY GUARANTEES

Mercury reduction regulations are currently being implemented in certain states such as Massachusetts, New Jersey, Wisconsin, North Carolina, and Connecticut. In addition, new power plants being planned are required to meet Maximum Achievable Control Technology (MACT) requirements for mercury. Carbon injection is being specified as the MACT technology for most of these new coal-fired power plants. Because of these state regulations and the new power projects, there is a significant amount of commercial activity for mercury control technologies. Bids are being requested from power companies for equipment to meet these emissions regulations and many require guarantees.

Guarantees of mercury control are being offered commercially in the marketplace today for many plant configurations and coal types. For mercury control technologies consisting of carbon injection systems followed by a particulate collector, such as a fabric filter or ESP, performance guarantees have been provided to firm customer specifications on commercial projects in various stages of development. These guarantees have included performance guarantees for mercury emissions and powdered activated carbon consumption that are contingent on coal type, coal mercury content, existing flue gas cleaning equipment, and plant operational data. The frequency of the compliance requirements; such as whether the guarantee would be based on hourly, daily or monthly average; would also influence the level of the guarantee. Generally, the process for developing guarantees for mercury control is the process that is common to development of guarantees for control of other air pollutants.

Vendors will guarantee a given emission rate for a specified range of coals having specified mercury content. They would generally not provide a collection efficiency guarantee since that would be progressively more difficult to meet the less mercury there is in the coal. For example, a coal with a mean mercury content of 0.15 ppm would typically be provided a guaranteed emission value between 1.5 – 7.0 micrograms Hg /Nm3 (corresponding to between 90 to 50 % removal efficiency respectively), all depending on the factors listed above. This issue could be simplified with a regulation that had a dual limit of a lower emission rate and a maximum efficiency. Given a longer compliance period, such as a yearly average, it is expected that guarantees for higher removal efficiencies would be provided for the vast majority of plants compared to shorter averaging periods.

Guarantees can be provided for the oxidation performance of mercury across an SCR. Mercury oxidation activity is adequately sustained with SCR catalyst over its lifetime for NO_x reductions. Based upon studies in the literature and data from vendor studies, the activity decline rate is similar to the De- NO_x decline rate. Coupled with predictive models for mercury oxidation that are being validated with full-scale data, performance guarantees can be provided.

At this point in the commercialization of mercury control equipment, the guarantees will likely be more conservative than in the coming few years. As with other air pollution control technologies such as wet scrubbers for SO_2 control and selective catalytic reduction for NO_x control, the more mercury control equipment that is installed and more experience gained, the tighter and more aggressive guarantees will become. In fact, some customers have not requested performance guarantees for criteria pollutant control technologies as the technologies are well established and able to easily meet the state and federal requirements.

In general, the guarantees provided for mercury controls are provided in the same manner that guarantees are provided for SO_2, NO_x and PM control technologies. The industry source will request a bid for a particular situation based on their regulatory requirements. The vendor will then submit a proposal based on the specific site characteristics defining the emission rate that is achievable and can be guaranteed for that specific application. After the control installation has been completed, testing will be performed to verify that the emissions guarantee has been met. The vendor may provide a 'make right' statement in the guarantee that the vendor will have a window of time, typically up to twelve months, to make adjustments to the technology if the guaranteed level was not initially satisfied. This is the general approach that is taken by vendors when guaranteeing a control technology installation whether it is for a SO_2, NO_x, PM or mercury control.

COMMERCIAL AVAILABILITY OF CONTROL TECHNOLOGIES

A number of air pollution control technologies for mercury control from power plants are commercially available or will be available by the end of the 2004. Mercury specific control technologies such as activated carbon injection systems are currently available and have already been used on full-scale systems for the power sector as well as for other industrial sectors. These systems can be applied to any plant configuration and coal type.

A number of mercury control approaches can be applied through the utilization of existing air pollution control equipment. These applications have the potential to provide immediate mercury control benefits and require little if any capital investment. For plants that already have an SCR installation, a promising technology that adds a reagent across an SCR catalyst is expected to be available in 2005. A U.S. patent was granted in October of 2003 that uses a chlorinating agent and ammonia to accomplish the simultaneous reduction of NO_x and oxidation of mercury over SCR catalyst. This technology has been successfully demonstrated in pilot work and will be tested on a much larger scale.

In addition, adding an additional layer of catalyst to existing SCR installations, and/or running existing SCR installations year-round, are viable options that increase the oxidized form of mercury making it easier to capture in existing downstream control equipment. This technology is immediately available to almost one-third of the coal-fired electric power sector due to the almost 100 GW of SCR installations for the NO_x SIP call, and is likely to pay for itself in the best plant configurations depending on the value of additional NO_x credited generated.

Other technologies such as the multipollutant ECO process are in the commercial demonstration stage. Pilot studies on smaller slip streams have been performed for 24 months and a 50 MW demonstration is in the beginning stages of operation. Based on successful commercial demonstration, the ECO technology is expected to be commercially available in late 2004.

WASTE STREAM DISPOSAL

Since the purpose of controlling emissions from coal-fired boilers is to reduce potential buildup of mercury compounds in lakes and streams and ultimately to protect public health, the stability of the captured mercury in the ash and other coal combustion byproducts (CCBs) is a critical component of the overall control scheme. The ICR program showed that currently approximately 30 tons per year of mercury is contained in CCBs. Pending mercury control regulations could result in an additional 20 to 40 tons per year of mercury in CCBs.

In the U.S., approximately 67% of all fly ash produced from utility coal combustion is disposed of in landfills or surface impoundments. The remaining 33% is used for a variety of commercial applications. There are approximately 600 waste disposal sites for CCBs in the U.S.; half are landfills and half are surface impoundments. Note here that CCBs include other waste streams such as bottom ash and scrubber sludge. A 1999 EPA study estimated that about half of the CCB landfills and a little less than a third of the surface impoundments have some type of liner, the most common type being compacted clay (Senior et al., 2002).

Volatilization of mercury from landfills was estimated by EPA to be small. To date, there has been no evidence based on laboratory leaching studies for leaching of large amounts of mercury from fly ash under landfill conditions. Leaching appears to be the most likely pathway for liberation of mercury from fly ash. Volatilization may be important for certain applications of fly ash as filler in concrete applications. Volatilization is, of course, the primary pathway for mercury release to the atmosphere if fly ash is used as a raw material in cement kilns. However, volatilization will be complete in this case.

PAC-injection applied to coal-fired boilers will result in the fly ash being mixed with a certain amount of mercury-containing sorbent. This material will be sent to land disposal or used in specific applications (assuming that the presence of the sorbent is compatible with the application). Since the mercury on the spent sorbent may be present in a different form than on fly ash, it is necessary to consider what might be the most likely routes for release of mercury in sorbent-fly ash mixtures and how sorbent-containing coal utilization byproducts (CUBs) should be tested.

Senior et al., (2002) evaluated samples of ash with activated carbon from two ADA-ES field demonstration programs. The Gaston sample (the product of a bituminous coal) had a high LOI and mercury content, in spite of the low sorbent injection rate, because most of the ash was removed upstream of the COHPAC baghouse by a hot-side ESP. Thus the sample had a relatively high proportion of sorbent. The Pleasant Prairie sample (the product of a subbituminous coal) had a low LOI and mercury content. Sorbent was injected upstream of an ESP and was combined with the full ash stream. The LOI and mercury content were much lower than the Gaston sample. Little or no mercury was detected with leaching tests including TCLP, SGLP (including 30- and 60-day leaching), and sulfuric acid leach (bituminous ash). Samples were also analyzed by CONSOL as part of a DOE program. They also found no leaching of mercury from activated carbon (Withum et al., 2002).

Although the ash with activated carbon appears to be highly stable, initial testing with a PRB ash determined that the presence of even trace amounts of activated carbon in the ash rendered the material unacceptable for use in concrete. Even though the Pleasant Prairie (PRB) ash conformed to the ASTM C-618 standard for Class C fly ash, it did not pass the Foam Index test that is also required for sale of this ash for use in concrete formulation. These are field tests used to determine the amount of Air Entrainment Additives needed to meet freeze-thaw requirements. This means that with activated carbon injection, the plant would not only lose revenues from ash sales, it would incur additional expenses to landfill the material.

For the multipollutant ECO technology, it is important to note that the mercury is removed from the co-product stream and is isolated for disposal. The stream is pumped through an activated carbon adsorption bed, which strongly adsorbs mercury compounds to the bed. The mercury is disposed of as a hazardous waste, and the spent activated carbon is replaced in the ECO process. It is estimated that the variable cost of mercury removal with activated carbon in the ECO process is $800 per pound of mercury, including the sorbent media and its disposal.

During the K-Fuel process, mercury is volatized and released from the coal in both the gaseous and liquid phases. The mercury and other heavy metals and pollutants are captured with carbon filters and disposed of at permitted disposal sites. The pre-combustion process captures these pollutants in a highly concentrated form compared to post-combustion technologies, thereby creating less waste. The process can achieve significant savings in waste disposal compared to post-combustion technology as tests have shown 5-10 times less solid waste disposal for pre-combustion technology versus post-combustion technology. The quality of the ash produced by the power plant is maintained as a usable, salable product.

RESOURCES FOR ENHANCEMENT OF EXISTING EQUIPMENT AND INSTALLATION OF NEW EQUIPMENT

SCR Catalyst: The SCR catalyst industry for coal-fired systems is a recent example of how quickly companies are able to build new production capacity in response to a significant jump in demand over a short period of time. The air pollution control industry installed close to 100 GW of SCRs over the last several years, with approximately 40 GW being installed in one year, in response to regulations requiring reductions in summer time NO_x emissions. This caused the catalyst manufacturers to more than double their SCR catalyst production to meet the market demand. SCR catalyst for enhanced SCR mercury oxidation is readily available due to overcapacity in this manufacturing sector. We estimate that extra SCR catalyst for SCR enhanced mercury oxidation approaches (extra layer and/or year-round operation) can be manufactured in one year. This would include all existing and projected SCR systems in 2010 under EPA's scenarios for existing rules plus the CAIR/IAQR. Installation manpower is not a limiting factor for catalyst addition.

Activated Carbon Injection: In general, the resources needed for the construction and operation of activated carbon injection technologies is significantly smaller than those required for the installation of SO_2 scrubbers and selective catalytic reduction units. The areas investigated for mercury control options includes the availability of sorbent (specifically activated carbon) and the availability of skilled labor assuming fabric filter installations along with carbon injection systems.

Activated carbon injection systems consists of a bulk-storage silo and twin blower/feeder systems to convey the activated carbon from the silo to the flue gas duct. The feeder system is typically designed to deliver 750 lb/hr of activated carbon. PAC is delivered in bulk pneumatic trucks and loaded into the silo. The silo is equipped with a bin vent bag filter to prevent activated carbon from escaping during the transfer process. From the two discharge legs of the silo, the reagent is metered by variable speed screw feeders into eductors that provide the motive force to carry the reagent to the injection point. Regenerative blowers provide the conveying air to suspend the activated carbon so that it can be transferred to the flue gas duct. A programmable logic controller (PLC) system is used to control the system operation and adjust injection rates. Figure 7 is a photograph of the sorbent silo and feeder train designed and installed to treat a 150 MW boiler. Hard piping carries the reagent from the feeders to distribution manifolds located on the ESP inlet duct, feeding the injection probes.

An activated carbon injection system can be installed in less than 6 months including the design, installation, and equipment testing which is significantly less than EPA estimated in their Engineering and Economic Factors Analysis (U.S. EPA, 2002). These are the installation times that have been typical for the current set of DOE demonstration projects. The injection systems; including the silo, feeders, controllers, etc., are commonly used in numerous industries, therefore, the production capacity far exceeds the incremental demand from any mercury rule for power plants. One silo company that was surveyed by ICAC indicated that they alone could produce 1500 silos in a single year. By comparison, EPA estimates that only 2 GW of ACI systems, approximately 4 coal-fired units, would be installed by 2010 assuming the simultaneous implementation of the Clean Air Interstate Rule (CAIR). Assuming that the CAIR rule were not implemented, EPA estimated that 63 GW of ACI systems, approximately 126 coal-fired units, would need to be installed. In either case, the supply of hardware for activated carbon injection systems can easily be accommodated by existing production capacity.

The most commonly used sorbent for mercury control has been activated carbon. For the past two decades, powdered activated carbon injection upstream of a baghouse has been successfully used for removing mercury from flue gases from municipal and hazardous waste combustors. Activated carbon is carbon that has been “treated” to produce certain properties such as surface area, pore volume, and pore size. Activated carbon can be manufactured from a variety of sources (e.g., lignite, peat, coal, wood). More commonly, steam is used for activation, which requires carbonization at high temperatures in an oxygen-lean environment. As some carbon atoms are vaporized, the desired highly porous activated carbon is produced. Commercially, activated carbons are available in a range of particle sizes, as well as other characteristics that are needed for a specific application.

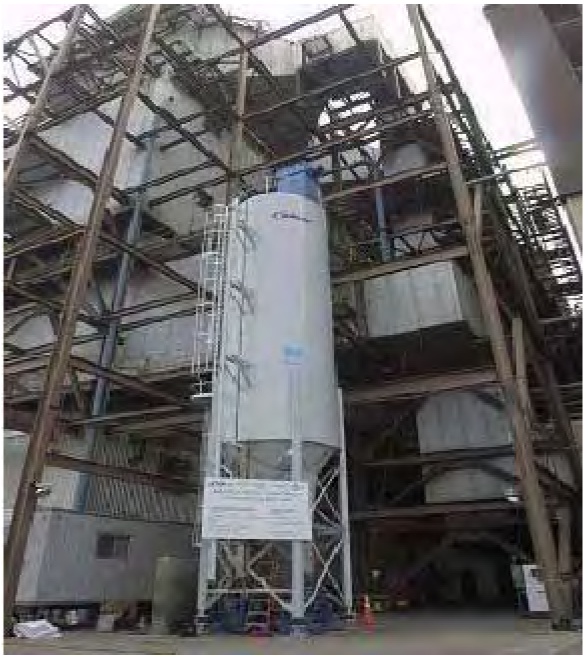

Figure 7. Carbon Injection Storage Silo and Feeder Trains for 150 MW.

A survey of the major suppliers of activated carbon in the U.S. and abroad demonstrates the amount of material that could be made available for this market with current production capacity (Durham, 2003). The results are presented in Table 4. The excess production capacity in the U.S. is approximately 62,000 tons per year. There is an additional 190,000 tons of AC that is available from China and Germany for this market. Chinese activated carbons are currently flooding the U.S. market and competing for the water treatment business.

The total excess capacity of activated carbon from foreign and domestic sources is approximately 250,000 tons per year. Table 5 presents an estimation of how many plants could be treated by this material in response to a mercury control regulation. The market share depends upon whether the activated carbon is used in conjunction with ESPs or fabric filters. The full-scale data indicate that mercury removal in the 50 to 70% range can be achieved with an ESP at a feed rate of 10 lb/MMacf, whereas 70 to 90% removal could be achieved with a fabric filter at one-third the feed rate. Therefore, if the 250,000 tons per year were applied to ESPs, then 120 of the 1,100 plants could be treated. However, if new fabric filters were installed on many plants, it would be possible to treat 400 units with this same amount of material without increasing the current production capacity.

Table 4. Estimates of Excess Production Capacity of Activated Carbon that could be Available for the U.S. Utility Market.

AC Source	Current excess capacity of AC production in Tons/year
NORIT Americas	22,500
Other U.S. Suppliers	40,000
Total U.S. Excess Capacity	**62,500**
Rheinbraun (Germany)	130,000
CarboChem (China)	60,000
Total Import Excess Capacity	**190,000**
Total U.S. and Import Excess Capacity	**252,500**

Table 5. Estimate of the Number of 250 MW Power Plants that could be Treated with Activated Carbon from Current Excess Capacity.

	Excess Capacity Tons/yr	ESPs (50-70%)	FFs (70-90%)
U.S. AC	62,000	30	99
Total U.S. plus Imports	252,000	120	400

A new mercury regulation would create a significant new market for activated carbon. All of the activated carbon manufacturers that were surveyed expressed a strong interest in investing significant capital in building new production facilities to provide sorbents for the utility market. In order to build new production capacity, between a two- to four-year period would be needed to expand production. However, all of the activated carbon suppliers said that they would be hesitant to invest capital resources to increase capacity based only on the promise of a new regulation. A decade or so ago, the AC industry increased capacity when EPA announced that they were going to tighten up drinking water standards. After the new capacity was added, EPA did not follow up with new regulations, which produced a glut of activated carbon. Some companies went out of business because of this, and the industry as a whole is just now recovering. As a result, it is unlikely that new AC production will move beyond the planning stages until there is the certainty of a regulation.

EPA's Economic and Energy Impact Analysis for the Proposed Utility MACT Rulemaking did not specify the number of fabric filters that would be installed along with the ACI systems to control mercury. The fabric filters, such as those used in the COHPAC and TOXECON systems would be added downstream of the existing particulate control device and would be installed following the sorbent injection system to collect the waste sorbent. The fabric filters that would be installed for these types of control applications would typically be smaller than the fabric filter that would be built as a dedicated particulate control device. EPA estimates that only 2 GW of ACI would be installed by 2010 assuming the simultaneous implementation of the CAIR rule. This would mean that approximately four units would need a fabric filter for mercury control. If for some reason the CAIR rule were not simultaneously implemented, EPA estimates that approximately 63 GW of ACI controls would be needed. Conservatively assuming that all 63 GW would need the smaller sized fabric filter would not provide a difficult installation challenge especially under the assumption that an additional 63 GW of SO2 (49 GW of scrubbers) and NOx (24 GW of SCR) controls would not be installed if CAIR were not implemented during the same timeframe.

ECO Technology: The *ECO technology* is expected to be installed and commissioned within 24 to 30 months after order placement. The components of this system, including the WESP, are commonly used for air pollution control. A picture of the 50 MW ECO commercial demonstration is provided in Figure 8. The predominant reagent used in ECO is ammonia. The ammonia can be supplied to the system in any form—anhydrous, aqueous of any concentration, or even from systems that generate ammonia from urea. All the ammonia that goes into the ECO system becomes part of the ammonia sulfate co-product (Boyle, 2003). Ammonia sulfate is a valued fertilizer both for its sulfur content and for its nitrogen content. The largest use of ammonia in the US is as a nitrogen fertilizer. Some of the ammonia is applied to fields directly, but most of it is converted to a more convenient form of nitrogen, either a liquid such as urea ammonium nitrate or a solid, such as granulated urea. The processing of ammonia into other forms of nitrogen is becoming more common as the difficulties of handling pure ammonia in an agricultural environment increase.

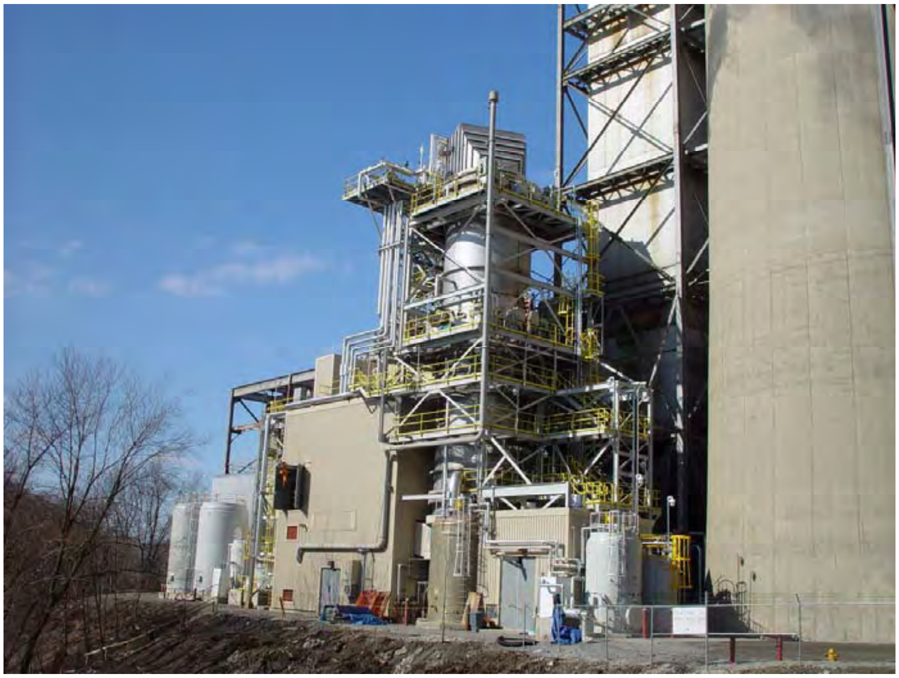

Figure 8. 50-MW ECO Commercial Demonstration Unit at FirstEnergy's R.E. Burger Plant

CONCLUSIONS

ICAC would recommend that a reduction of 50-70% of current emission levels in the 2008 to 2010 timeframe be targeted and that it is achievable via enhancements in existing SCR and wet FGD pollution control technologies as well as installation of mercury specific sorbent injection systems. ICAC would also recommend including flexible mechanisms in the regulation that encourage innovation while providing clear goals and meaningful reductions. This type of approach would provide cost effective solutions and minimize impacts on generation mix.

Flexible mechanisms are important for mercury control technology for a variety of reasons. Some examples of these types of concepts include but are not limited to the following: early reduction incentives, market based approaches, capital recovery programs, plant wide averaging, safety valves or other approaches. The cost of the control technology is related to the size of the plant treated so that two plants of identical size but with a factor of ten differences in emissions would have almost the same capital and operating costs. Therefore, the cost per pound of mercury removed would be ten times higher for the low-emission plant. Flexible mechanisms would provide a means to level the playing field and actually create incentives for the power companies to treat the higher emitting plants, thus, making the largest amount of reductions in total mercury emissions while minimizing costs.

These incentives would also alleviate some of the issues related to differences and uncertainties in performances due to plant-by-plant variations in coal characteristics and equipment design. This will significantly reduce risk for both the air pollution control technology vendor and the power company purchasing mercury control technology. Certain incentives would mitigate risk and reward early compliance for plants that install equipment. This would increase the experience base which will decrease uncertainty and make it possible to provide more aggressive performance guarantees.

REFERENCES

Boyle, P.D., D. Steen, A. DoVale (2003). "Commercial Demonstration of ECO® Multi-Pollutant Control Technology," ICAC Forum 03: Multi-Pollutant Emission Controls and Strategies, Nashville, TN, October 14-15.

Bustard, C.J., S.M. Sjostrom, and R. Chang (1997). "Predicting COHPAC Performance," presented at EPRI-DOE-EPA Combined Utility Air Pollutant Control Symposium, Washington, D.C., August 25-29.

Bustard, C.J., M. Durham, C. Lindsey, T. Starns, K. Baldrey, C. Martin, R. Schlager, S. Sjostrom, R. Slye, S. Renninger, L. Monroe, R. Miller and R. Chang (2002). "Full-Scale Evaluation of Mercury Control with Sorbent Injection and COHPAC at Alabama Power E.C. Gaston," special edition *JAWMA*, June.

Bustard, C.J., M. Durham, T. Starns, C. Martin, R. Schlager, C. Lindsey, K. Baldrey, L. Monroe, T. Coughlin, D. Johnson, S. Renninger and R. Chang (2002). "Full-Scale Evaluation of Sorbent Injection for Mercury Control on Coal-Fired Power Plants," Air Quality III Conference, Arlington, VA, September 9-12.

Bustard, C.J., M. Durham, T. Starns, C. Martin, R. Schlager, C. Lindsey, K. Baldrey, S. Sjostrom, S. Renninger and R. Chang (2002). "Full-Scale Evaluation of Sorbent Injection for Mercury Control on Coal-Fired Power Plants," submitted for presentation at the Nineteenth Annual International Pittsburgh Coal Conference, Pittsburgh, PA, and September 23-27.

Durham, M. (2003) "Status and Capabilities of Mercury Control Technology: Policy Implications"; Air Quality IV, Washington D.C., September 22.

Durham, M., C.J. Bustard, T. Starns, S. Sjostrom, C. Lindsey, C. Martin, R. Schlager, R. Chang, S. Renninger, L. Monroe, M. Berry, and D. Johnson (2003). "Full-Scale Results of Mercury Control by Injecting Activated Carbon Upstream of ESPs and Fabric Filters," Power-Gen 2003, Las Vegas, NV, December 9-11.

Durham, M., C.J. Bustard, T. Starns, C. Martin, R. Schlager, C. Lindsey, K. Baldrey, and R. Afonso (2002). "Full-Scale Evaluations of Sorbent Injection for Mercury Control on Power Plants Burning Bituminous and Subbituminous Coals," Power-Gen 2002, Orlando, FL, December 10-12.

Durham, et al (2001). "Field Test Program to Develop Comprehensive Design, Operating and Cost Data for Mercury Control Systems on Non-Scrubbed, Coal-Fired Boilers," Presented at 94th Annual A&WMA Conference and Exhibition, Orlando, FL, June.

Durham, M.D., C.J. Bustard, R. Schlager, C. Martin, S. Johnson, S. Renninger (2001). "Controlling Mercury Emissions from Coal-Fired Utility Boilers: A Field Test," *EM, Air & Waste Management Association, pp 27 – 33, July 2001.*

Hassett, D.J., L.V. Heebink, and D.F. Pflughoeft-Hassett (2002). "Potential for Mercury Release from Coal Combustion By-Products," Air Quality III Conference, Arlington, VA, September 9-12.

Laudal, D.L., J.S. Thompson, J.H. Pavlish, L.A. Brickett, P. Chu, R.K. Srivastava, C.W. Lee, and J.D. Kilgroe (2002). "Evaluation of Mercury Speciation at Power Plants Using SCR and SNCR NO_x Control Technologies," Air Quality III Conference, Arlington, VA, September 9-12.

Lee, C., R. Srivastava, B. Ghorishi, T. Hastings, and F. Stevens (2003). "Study of Speciation of Mercury under Simulated SCR NO_x Emission Control Conditions," Combined Power Plant Air Pollutant Control: Mega Symposium, Washington, DC, May 19-22.

Lindau, L. (1983) "Mercury Sorption to Coal Fly Ash," *Staub-Reinhaalt. Luft* , v. 43 p. 166.

Senior, C., C.J. Bustard, M. Durham and K. Baldrey (2002). "Characterization of Fly Ash from Full-Scale Demonstration of Sorbent Injection for Mercury Control on Coal-Fired Power Plants," Air Quality III Conference, Arlington, VA, September 9-12.

Senior, C., C.J. Bustard, K. Baldrey, T. Starns, and M. Durham (2003). "Leaching Studies of Fly Ash from Full-Scale Demonstration of Sorbent Injection for Mercury Control on Coal-Fired Power Plants," The Mega Meeting: Power Plant Air Pollution Control Symposium, Washington, D.C., May 19-22.

Sjostrom, S., C.J. Bustard, M. Durham, and R. Chang (2002a). "Mercury Removal Trends and Options for Coal-Fired Power Plants with Full-Scale ESPs and Fabric Filters," Nineteenth Annual International Pittsburgh Coal Conference, Pittsburgh, PA, September 23-27.

Sjostrom, S., T. Ebner, R. Slye, R. Chang, M. Strohfus, J. Pelerine, and S. Smokey (2002b). "Full-Scale Evaluation of Mercury Control at Great River Energy's Stanton Generating Station using Injected Sorbents and a Spray Dryer/Baghouse", Air Quality III Conference, Arlington, VA, September 9-12.

Sjostrom, S., R. Chang, T. Hagley, A. Rudek and J. Skelton, T. Ebner and R. Slye (2003). "Full-Scale Evaluation Of Mercury Control Across A Wet Particulate Scrubber." Presented at the Combined Power Plant Air Pollutant Control Symposium, May 19-22.

Starns, T., C.J. Bustard, M.D. Durham, C. Lindsey, C. Martin, R. Schlager, B. Donnelly, S. Sjostrom, P. Harrington, S. Haythornthwaite, R. Johnson, E. Morris, R. Chang and S. Renninger (2002). "Full-Scale Test of Mercury Control with Sorbent Injection and an ESP at Wisconsin Electric's Pleasant Prairie Power Plant," 95th A&WMA Annual Meeting, Session AE-1, Baltimore, MD, June 23-27.

U.S. EPA, Office of Research and Development (2002). "Engineering and Economic Factors Affecting the Installation of Control Technologies for Multipollutant Strategies," EPA-600/R-02/073, October.

U.S.EPA, Clean Air Markets Division (2004). “Economic and Energy Impact Analysis for the Proposed Utility MACT Rulemaking,” Air Docket, January 28.

Withum, J.A., A.M. Schwalb, and R.M. Statnick (2002). “Characterization of Coal Combustion By-Products for the Re-Evolution of Mercury into Ecosystems,” Air Quality III Conference, Arlington, VA, September 9-12.

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Senate Democratic Policy Committee

Hearing on EPA Proposal to Regulate Mercury Emissions from Power Plants

Testimony of the Institute of Clean Air Companies (ICAC)
Presented by David C. Foerter, Executive Director

Friday, July 9, 2004

Good morning. I'm Dave Foerter, Executive Director for the Institute of Clean Air Companies ("ICAC" or "the Institute").

The Institute is the nonprofit, national association of companies that manufacture, supply, and service air pollution control and monitoring systems for a broad range of air pollutants, including mercury from power plant and industrial sources. The Institute represents a diverse group of approximately eighty companies dedicated to air pollution control. As such, the Institute represents the full range of competing technologies, rather than any single technology. In the few minutes I have here this morning, I'll begin with the "bottom-line."

Our industry believes that a 50 to 70 percent reduction from current mercury emissions of 48 tons per year is feasible by 2008 to 2010. As a result, over the next 4 to 6 years, it is reasonable and cost-effective to achieve a utility mercury budget of 14 to 24 tons. The air pollution control industry has both the technology and the resources to exceed the magnitude of NO_x, SO_2, $PM_{2.5}$, and mercury reductions, and in a shorter time frame than proposed by the U.S. Environmental Protection Agency (EPA).

It is important to remind ourselves that air pollution control technology markets have historically worked well. Studies show that the certainty of regulatory drivers spurs technical performance and cost improvement. And total costs fall dramatically as control technology moves from R&D to full-scale commercialization. It is reasonable to assume that even with the tremendous technological achievements already made, the traditional successful operation of the air pollution control market will also apply to the development and enhancement of mercury emission controls. The key to well-functioning markets is regulatory certainty. If the goal is technological innovation, then it is important to enact a clear, certain, performance-based mandate. While the Institute advocates flexibility in meeting control requirements, that compliance flexibility should be considered only after setting emissions budgets that adequately protect public health and make use of the capabilities of control technology.

One technology in particular, activated carbon injection, has been used for at least a decade in the waste to energy industry to achieve mercury reductions of at least 80 to 90 percent. This technology has been successfully transferred to the power sector for commercial use. Activated carbon injection provides a relatively low cost solution, with very little capital investment and relatively low operating costs. In addition, control performance can be increased and operating cost decreased, if activated carbon injection is coupled with fabric filter particulate control devices. In an intensive effort over the last five years, this technology has been rigorously demonstrated through the Department of Energy's (DOE) Clean Coal Power Initiative at full scale on electric power plants, with additional demonstrations to be completed by 2005. The demonstrations identified and addressed power sector mercury control issues, but, more importantly, dramatically removed potential barriers and enhanced the technology. R&D has already matured to full-scale demonstrations and are applicable to a wide range of coal types and existing equipment configurations. Many of these project teams include utility end-users as well as technology developers, which indicates the wide-ranging, cooperative effort underway. The success of this work and other applications, have now all but obscured the 1999 Information Collection Request (ICR) data that was used by EPA to propose the MACT floor. EPA's data shows that existing controls not intended to reduce mercury, had a side-benefit of removing other pollutants, including mercury. In fact, reliance on the 1999 ICR data promotes switching between coal types to achieve compliance, while the more current data shows economical compliance can be achieved without coal switching.

As we have informed EPA and others, a growing number of companies offer commercially available mercury control technologies for sale to the electric power sector. In fact, there are an increasing number of electric utilities actively procuring these technologies and services. Several other technologies are in various stages of development and commercial availability, ready to compete as compliance options under the Utility MACT program. We believe that Congress or EPA does not have to pick technology winners and losers; the marketplace is adept at doing so. The course of technology development is too unpredictable to say what the best approach will be and experience strongly indicates that there will not be one universal approach.

The rapid development of mercury control technologies make it feasible for the electric power sector to cost effectively reduce significantly more mercury emissions than called for under the proposed Utility MACT program. Assuming the implementation of a MACT program requiring control at each plant, it is estimated that a 50 percent reduction from the current emission level of 48 tons of mercury down to 24 tons is achievable. To achieve greater levels of control, there will be performance differences at each site due to differences in coal, equipment, and flue gas characteristics. At some power plants mercury control technology can reduce mercury emissions by 90 percent or greater. Therefore, if a mercury control program included compliance flexibility it is expected that a 70 percent reduction in emissions (down to 14 tons of emissions) is achievable.

Even within the MACT program constraints, EPA can provide compliance flexibility to achieve a high level of mercury control under the Utility MACT timeline without negatively affecting generation. Some of these mechanisms have been used in previous EPA regulations, both MACT and acid rain rules, such as: long term averaging, limits that specify a percent removal and emission rate, early reduction incentives such as those used under the Title IV NO_x provisions or Section 112 (i) (5) and (6), or a safety net approach that requires significant reduction with some flexibility for difficult applications. It is important that flexibility include the performance that is achievable by technology, rather than a prescription for a particular technology.

The air pollution control industry has already achieved commercial readiness of mercury control and measurement technologies, even without the certainty typically provided by regulatory or legislative market drivers. Mercury control technology is available today at the reasonable cost of 0.1 to 0.3 cents per kW-hr, compared to and average retail rate of 8 cents per kW-hr. Mercury control technologies are currently available for a range of coals and equipment and will be available for every utility configuration and every coal type in the near future. Mercury reductions of 50 percent (24 tons of emissions) are achievable by 2008 to 2010, and up to a 70 percent (14 tons of emissions) would be achievable by all utilities if there were some flexibility in regulation or legislation.

On behalf of the more than 130,000 men and women in our nation that work to supply air pollution control and monitoring technology for stationary sources, we congratulate efforts to develop meaningful and flexible approaches to control emissions from the electric power sector. Dollars spent on compliance are recycled in the economy, generating jobs in construction, materials fabrication, and engineering. The Institute predicted that multi-pollutant control requirements would create 300,000 new U.S. jobs.

Thank you for this opportunity to testify. I look forward to your questions.

# # #

For more information go to www.icac.com or contact ICAC at 202.457.0911

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Commercial Electric Utility Mercury Control Technology Bookings

Air pollution control vendors are reporting booking new contracts for mercury control equipment for more than two dozen power plant boilers. The contracts for commercial systems are attributed to federal and state regulations, including new source permit requirements and consent decrees, which specify high levels of mercury capture. Below is a summary of the mercury control equipment that has been procured to date. Highlighted units are currently in operation. **Last Update: 09-18-2007**

	Plant Size (MW)	Location	Prime OEM Contractor	Coal	APC Configuration	Hg Control	New Plant or Retrofit	Regulatory Driver
1	90 MW ea. 270 Total	**Midwest**	Wheelabrator (Norit/ADA-ES)	PRB	TOXECON	ACI	Retrofit	Consent Decree
2	250	**East**	Wheelabrator	Bituminous	SDA/FF	ACI	Retrofit	State Regulatory
3	250	**East**	Wheelabrator	Bituminous	SDA/FF	ACI	Retrofit	State Regulatory
4	650	**East**	Wheelabrator	Bituminous	ESP	ACI	Retrofit	State Regulatory
5	740	**Midwest**	B&W (ADA-ES)	PRB	SDA/FF	ACI	New Plant	New Construction Permit
6	550	**Midwest**	B&W (ADA-ES)	PRB	SDA/FF	ACI	New Plant	New Construction Permit
7	350	**West**	B&W (ADA-ES)	PRB	SDA/FF	ACI	Retrofit	Consent Decree
8	350	**West**	B&W (ADA-ES)	PRB	SDA/FF	ACI	Retrofit	Consent Decree
9	800	**West**	B&W (ADA-ES)	PRB	SDA/FF	ACI	New Plant	New Construction Permit
10	350	**East**	ADA-ES	Bituminous	ESP	ACI	Retrofit	Consent Decree
11	350	**East**	ADA-ES	Bituminous	ESP	ACI	Retrofit	Consent Decree
12	204	**Midwest**	Dustex	PRB	TOXECON	ACI	Retrofit	Consent Decree
13	375	**East**	Wheelabrator	Bituminous		ACI	Retrofit	Consent Decree

14	650	**Midwest**	Alstom (ADA-ES)	PRB	SDA/FF	ACI	New Plant	New Construction Permit
15	156 MW ea. 315 Total	**Midwest**	Powerspan	Bituminous	Multi-pollutant	ECO	Retrofit	Construction Permit
16	750	**Midwest**	Wheelabrator	High Sul. Bit	ESP/WFGD/WESP	ACI	New Plant	Construction Permit
17	680	**South**	Alstom (ADA-ES)	PRB	SDA/FF	ACI	New Plant	Construction Permit
18	107	**East**	BPI	Bit./Bio-Mass	FT-SNCR/CDS/FF	ACI	Retrofit	DOE Demo.
19	860	**South**	BPI	Lignite	SCR/FF/WFGD	ACI	New Plant	Construction Permit
20	860	**South**	BPI	Lignite	SCR/FF/WFGD	ACI	New Plant	Construction Permit
21	220	**West**	B&W (ADA-ES)	PRB	SDA/FF	ACI	New	Construction Permit
22	575	**Southwest**	B&W (STC)	West.Bit/Sub. Bit. Blend	HS-ESP/FF/WFGD	ACI	Retrofit	Construction Permit
23	575	**Southwest**	B&W (STC)	West.Bit/Sub. Bit. Blend	HS-ESP/FF/WFGD	ACI	Retrofit	Construction Permit
24	335	**Northeast**	ADA-ES	Bituminous	Cold-Side ESP	ACI	Retrofit	Voluntary Regional Emission Abatement Plan
25	880	**South**	Wheelabrator	PRB	ESP/FF (TOXECON)	ACI	Retrofit	Voluntary Regional Emission Abatement Plan
26	350	**Midwest**	Hamon (ADA-ES)	PRB	SCR/FF	ACI	Retrofit	State Regulatory
27	650	**Southwest**	ADA-ES	PRB	ESP/FF	ACI	Retrofit	Voluntary Regional Emission Abatement Plan
28	628	**Southwest**	ADA-ES	RPB	ESP/FF Parallel Flow	ACI	Retrofit	Voluntary Regional Emission Abatement Plan
29	855	**Southwest**	ADA-ES	Lignite/PRB	ESP/WFGD	ACI	Retrofit	Voluntary Regional Emission Abatement Plan
30	670	**Midwest**	Alstom/ADA-ES	PRB	SCR/FF/WFGD	ACI	Retrofit	Construction Permit of new unit

31	850	**Midwest**	Alstom/ADA-ES	PRB	SCR/FF/WFGD	ACI	New	Construction Permit
32	167	**East**	Sorbent Tech	E- Bitum	ESP/WFGD	ACI	Retrofit	Consent Decree
33	108	**Midwest**	Dustex	PRB	TOXECON	ACI	Retrofit	Consent Decree
34	159	**Midwest**	NORIT	PRB	ESP	ACI	Retrofit	CAMR
35	348	**Midwest**	NORIT	PRB	ESP	ACI	Retrofit	State Regulatory
36	237	**Midwest**	NORIT	PRB	ESP	ACI	Retrofit	State Regulatory
37	347	**Midwest**	NORIT	PRB	ESP	ACI	Retrofit	State Regulatory
38	341	**Midwest**	NORIT	PRB	ESP	ACI	Retrofit	State Regulatory
39	566	**Midwest**	NORIT	PRB	ESP	ACI	Retrofit	State Regulatory
40	561	**Midwest**	NORIT	PRB	ESP	ACI	Retrofit	State Regulatory
41	850	**Midwest**	NORIT	PRB	ESP	ACI	Retrofit	State Regulatory
42	850	**Midwest**	NORIT	PRB	ESP	ACI	Retrofit	State Regulatory
43	359	**Midwest**	NORIT	PRB	ESP	ACI	Retrofit	State Regulatory
44	385	**Midwest**	NORIT	PRB	ESP	ACI	Retrofit	State Regulatory
45	281	**Midwest**	NORIT	PRB	ESP	ACI	Retrofit	State Regulatory
46	551	**Midwest**	NORIT	PRB	ESP	ACI	Retrofit	State Regulatory
47	400	**Southwest**	Alstom/ADA-ES	PRB	SDA/FF	ACI	New	Construction Permit
48	495	**Alberta Canada**	B&W/NORIT	Can. Sub-Bit.	SDA/FF	ACI	New	Construction Permit
49	800	**Midwest**	Wheelabrator	E. Bit	Lime Inj./ESP/WFGD/WESP	ACI	New	Construction Permit

50	800	**Midwest**	Wheelabrator	E. Bit	Lime Inj./ESP/WFGD/WESP	ACI	New	Construction Permit
51	350	**Midwest**	ADA-ES	PRB	ESP	ACI	Retrofit	Construction Permit
52	568	**Southwest**	AESI/ADA-ES	Lignite	CFB Boilers/SNCR/ACI/CDS-DFGD/FF	ACI	New	Construction Permit
53	248	**Midwest**	ADA-ES	PRB	ESP	ACI	Retrofit	State Regulatory
54	590	**Midwest**	ADA-ES	PRB	ESP	ACI	Retrofit	State Regulatory
55	608	**Midwest**	ADA-ES	PRB	ESP	ACI	Retrofit	State Regulatory
56	110	**Midwest**	ADA-ES	PRB	ESP	ACI	Retrofit	State Regulatory
57	272	**Midwest**	ADA-ES	PRB	ESP	ACI	Retrofit	State Regulatory
58	375	**Midwest**	ADA-ES	PRB	ESP	ACI	Retrofit	State Regulatory
59	100 ea. 200 Total	**Northeast**	Clyde Bergemann EEC	PRB	Dry Injection/FF	ACI	Retrofit	State Regulatory
60	200 ea. 400 Total	**Northeast**	Clyde Bergemann EEC	PRB	Dry Injection/FF	ACI	Retrofit	State Regulatory
61	200 ea. 400 Total	**Northeast**	Clyde Bergemann EEC	PRB	Dry Injection/FF	ACI	Retrofit	State Regulatory
62	300	**Midwest**	Allied/ADA-ES	PRB	CDS/FF	ACI	Retrofit	Construction Permit

ReACT Process Evaluation at the North Valmy Station

John Gilbert	Sierra Pacific Power
Chuck Dene	EPRI
Kevin Jackson	Shaw Env. & Infrastructure
Shyo Miyagawa	J-Power EnTech

ReACT Slip Stream Testing

- Objective:
  - Evaluate Performance on US Coals in 2.5 MW Slipstream
- Project Funders
  - Sierra Pacific Resources (Host)
  - Ameren
  - Consumers Energy
  - Integrys Energy
  - MidAmerican
  - Salt River Project
- J-Power EnTech (Process Supplier)
- Shaw Environmental (Test Contractor)

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ReACT™ Process

Multi-pollutant capture in an all-solid process with potential for sulfur/sulfuric acid recovery

2nd generation Bergbau Forschung (Mitsui) process

Advantages

- Dry process
- High SO_2 & Hg Control
- Saleable by-product

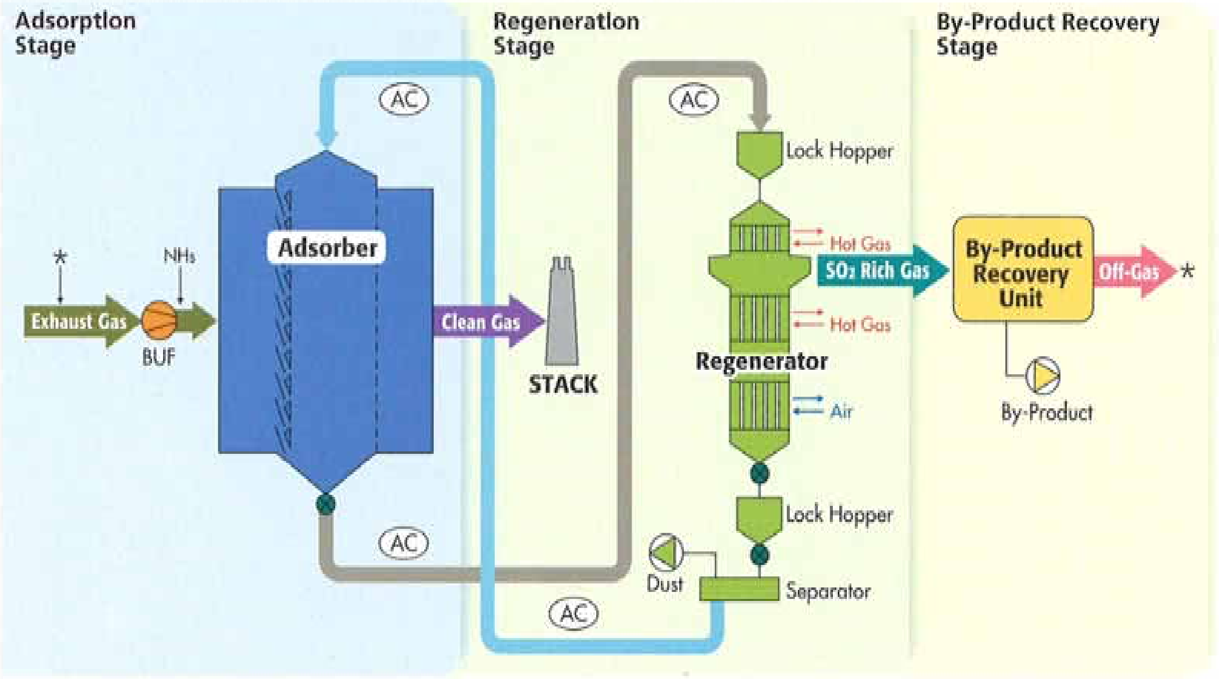
Enhancements

- –Improved carbon bed material ➔ reduced attrition & fire danger
- –Reduced vessel requirements

Performance

- •97-99+% ΔSO_2
- •25-48% ΔNO_X

Removals best @ S<2%


Adsorption Stage
Regeneration Stage
By-Product Recovery Stage
AC
AC
Lock Hopper
Hot Gas
SO₂ Rich Gas
Hot Gas
By-Product Recovery Unit
Off-Gas
*
*
NH₃
Adsorber
Exhaust Gas
BUF
Clean Gas
STACK
Regenerator
Air
By-Product
AC
Lock Hopper
Dust
Separator
AC

9,500 Nm³/hr or 5,900 scfm

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Valmy Coal Properties for ReACT Testing

North Valmy Unit 1 – 254 MW (Source)
Unit 2 – 267 MW

	Sub-Bituminous	Bituminous
H_2O	17.94%	9.30%
C	56.12%	65.81%
H	3.64%	4.54%
N	1.14%	1.14%
Cl	0.00%	0.02%
S	0.37%	0.46%
Ash	8.67%	10.15%
O	12.14%	8.62%
Hg	0.023 ppm	0.050 ppm
HV	9,670 Btu/lb	11,330 Btu/lb

Sierra Pacific EnTech

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Test Plan

	SV (1/hr)	RT (hr)	AC Load ($mgSO_2/gAC$)	Inlet SO_2 (ppm)	Coal
1-1	350	80	56	500	Sub-Bit
1-2	430	80	69	500	Sub-Bit
1-3	350	120	84	500	Sub-Bit
1-4	500	80	80	500	Sub-Bit
1-5	350	80	56	500	Sub-Bit
2-1	350	80	56	500	Bit
2-2	500	80	80	500	Bit
2-3	350	120	84	500	Bit
2-4	350	80	56	500	Bit
2-5	350	80	56	500	Bit
3-1	350	80	80	1400	Bit
3-2	350	40	80	1400	Bit
4-1	350	80	78	500-1400	Bit

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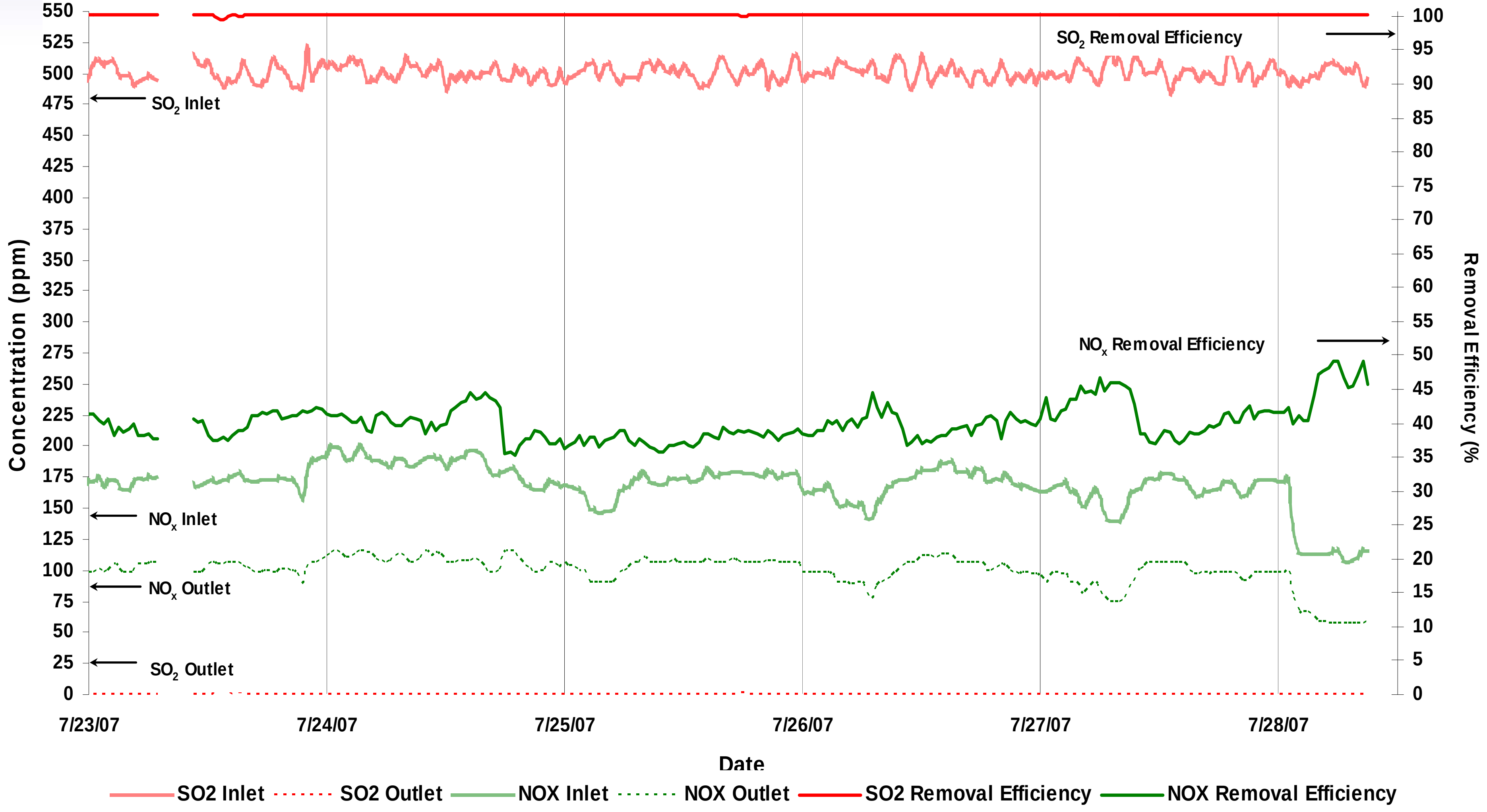
Baseline Sub-Bit Coal

500 ppm SO_2, SV=350, RT=80



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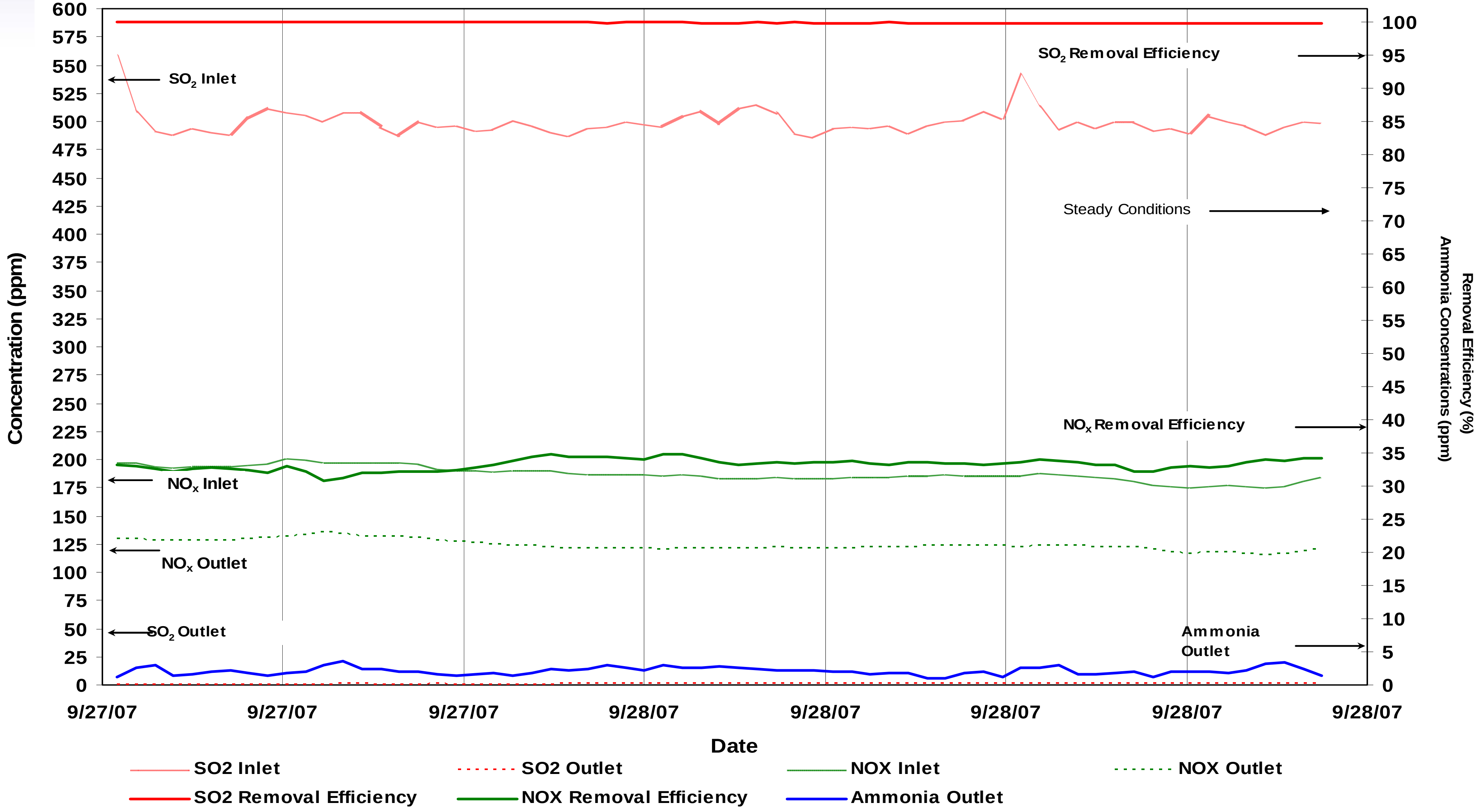
Baseline Western Bituminous Coal

500 ppm SO_2, SV=350, RT=80



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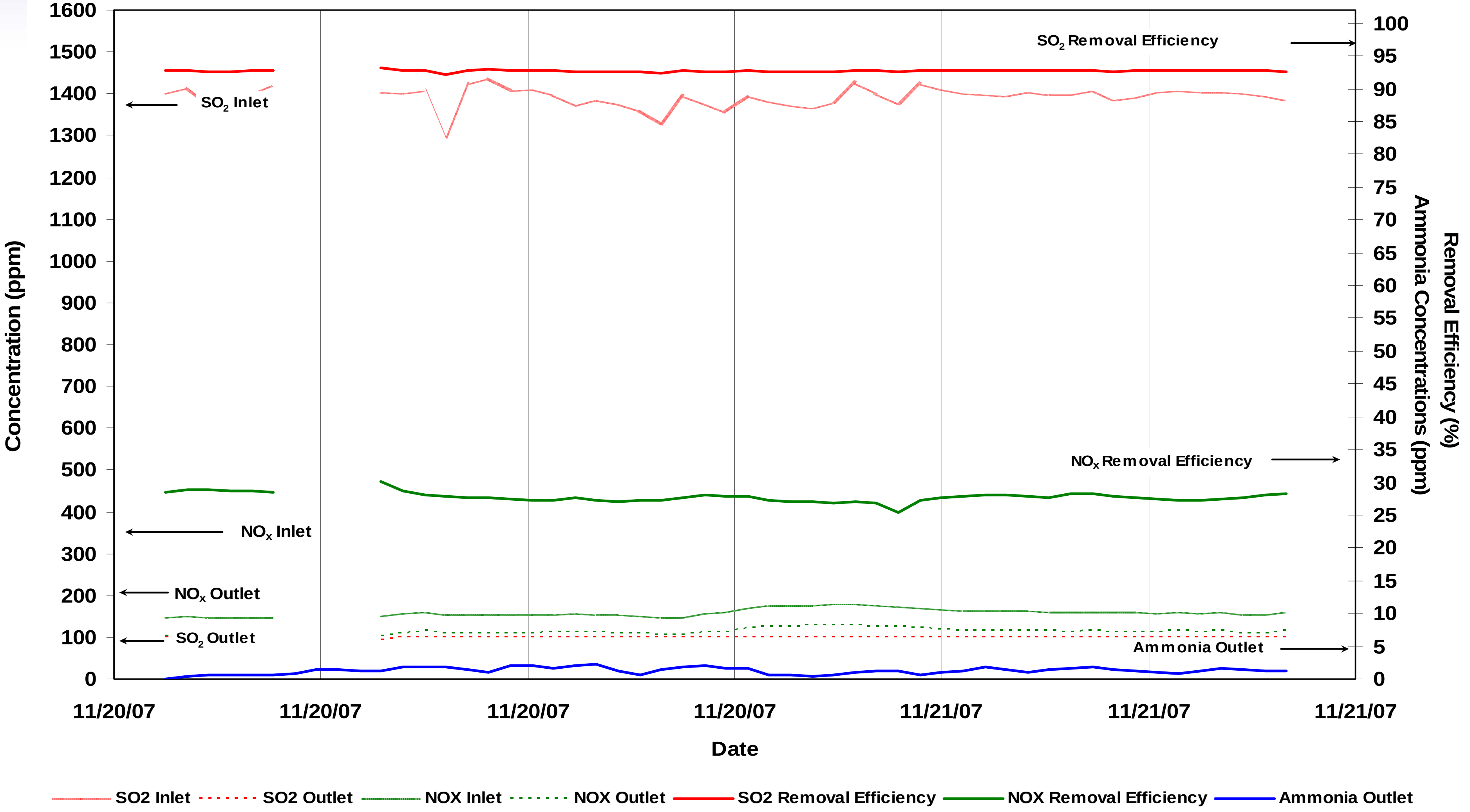
Western Bituminous Test 3-2

1400 ppm SO_2, SV=350, RT=40



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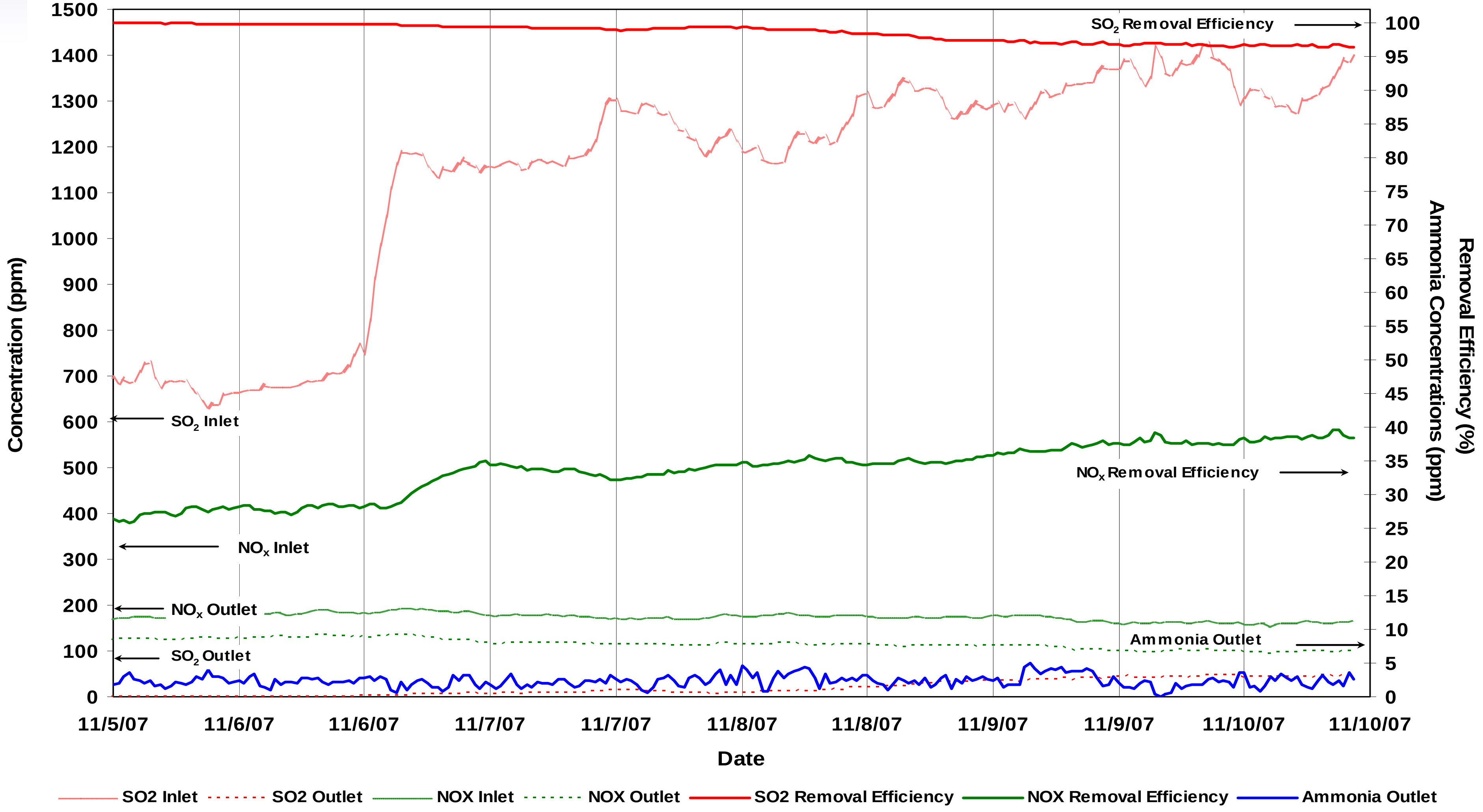
Transient Test

500-1400 ppm SO_2, SV=350, RT=80



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Removal Efficencies

Test	SO_2 Removal	NO_X Removal	Hg Removal
1-1	99.96	40.0	98.6
1-2	99.7	27.6	99.6
1-3	99.7	28.6	99.4
1-4	98.1	26.2	99.0
1-5	99.8	38.0	99.1
2-1	99.9	33.2	98.8
2-2	97.6	25.7	-
2-3	99.8	37.8	97.1
2-4	99.9	37.7	-
2-5	99.96	34.4	99.0
3-1	97.2	48.4	99.3
3-2	92.6	27.6	97.0
4-1	99.9	27.8	-

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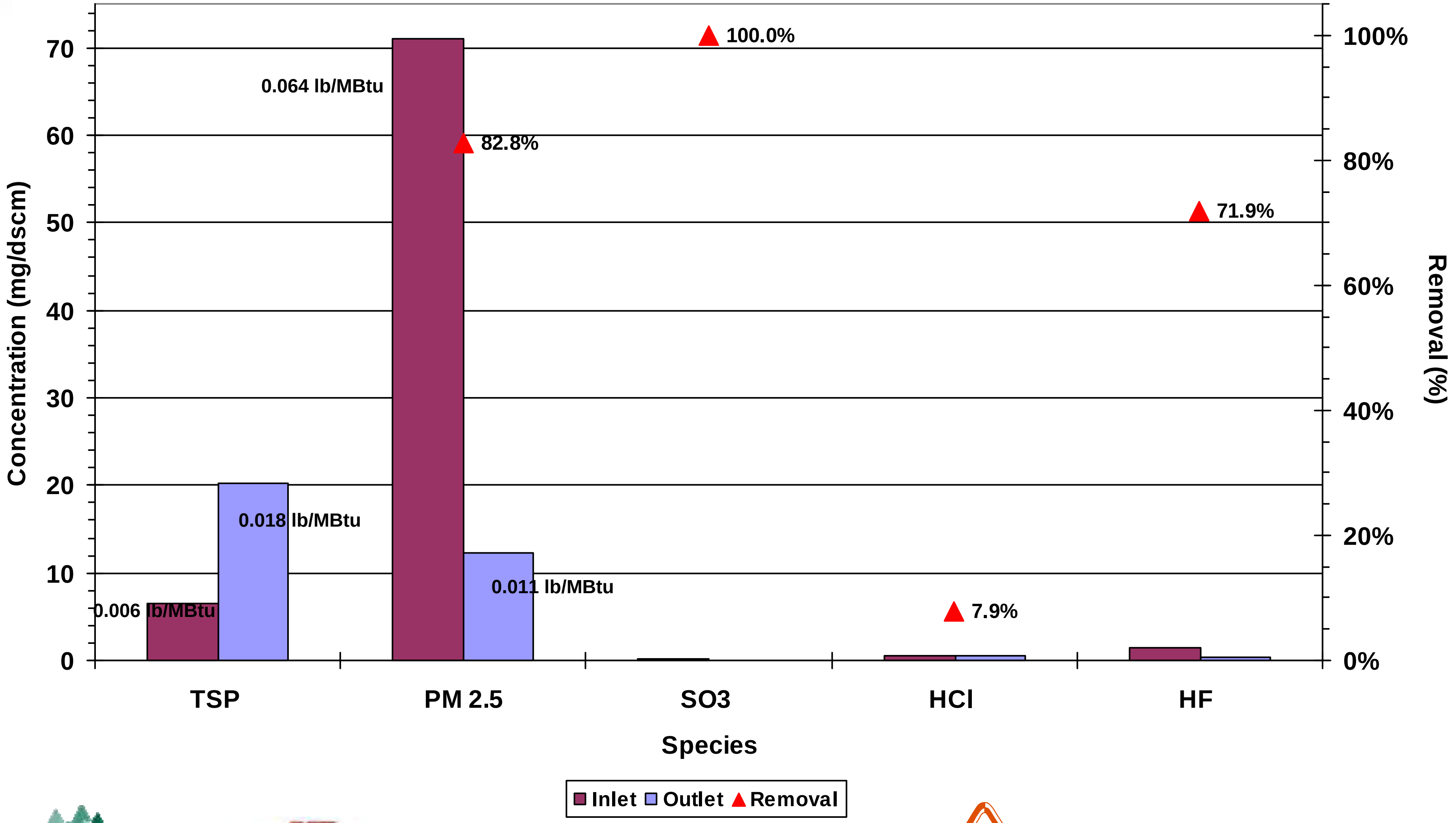
ReACT Baseline PM & Acid Gas Results



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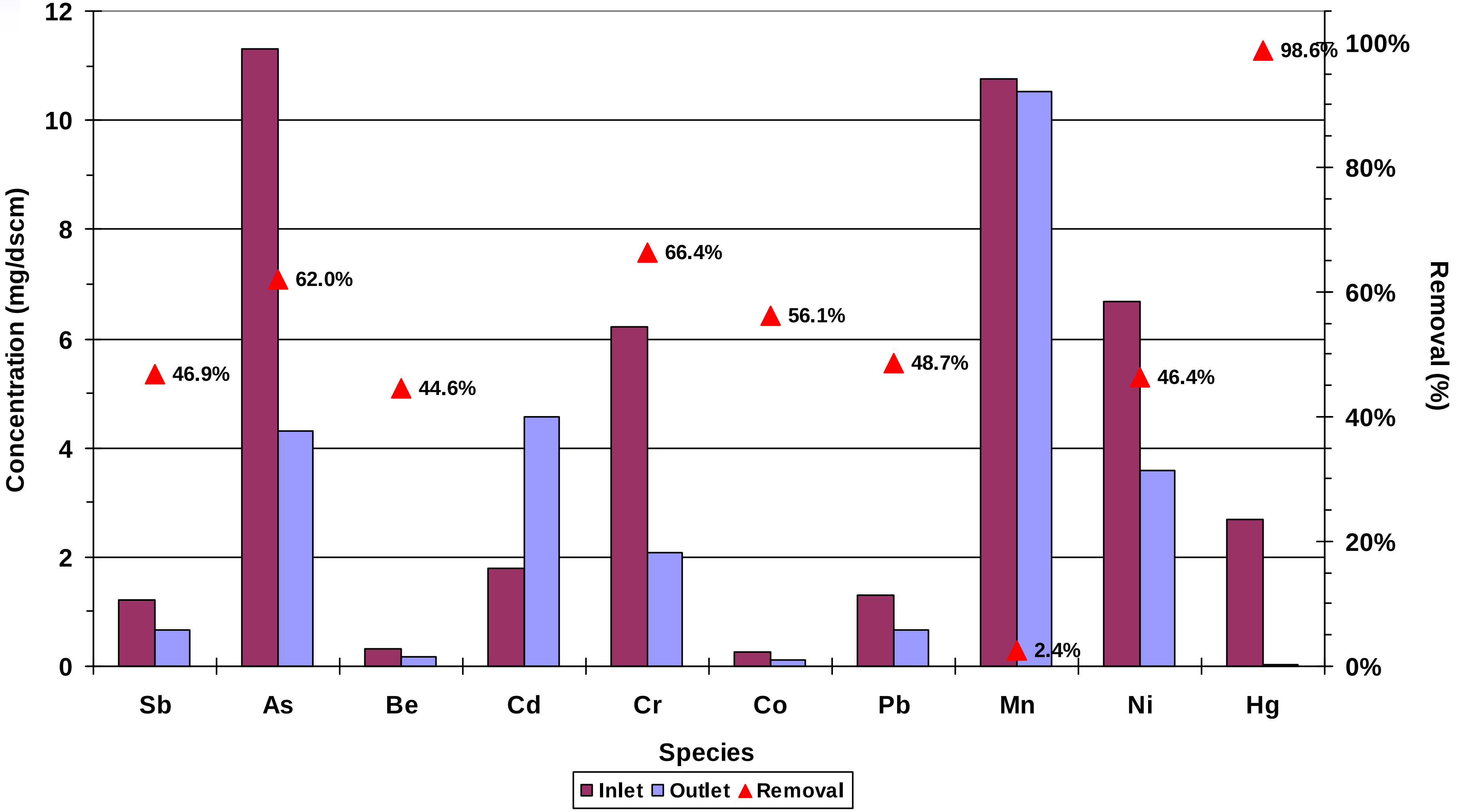
ReACT Baseline Metals Removals



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Summary

	Reported	Valmy Results
SO_2	>95%	97-99.9%
NO_X	20-80%	25-48%
Hg	90%	97-99%

- Important Parameters for SO_2 Removal:
  - RT, AC Loading, NH_3/SO_2 molar ratio
- Important Parameters NO_X Removal:
  - SV, RT, AC Loading, NH_3/SO_2 molar ratio
- Results for SO_2, NO_X, and Hg were reproducible between the two Baseline Tests. Results for other metals were approaching analytical detection limits.
- System operated almost 3,000 hours with no significant operational problems.

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ReACT™ Economic Evaluation

Coal	Comparison SOx, NOx & Hg	Total Capital Requirement ($/net kW)	Levelized Annual Cost (mills/kWh)
PRB (0.48%S)	ReACT™ System	$188	9.02
	OFA/CI/LSD/FF	$204	10.6
Bituminous (2.6%S)	ReACT™ System	$346	16.4
	SCR/LSFO	$307	15.0
Lignite (1.0%S)	ReAct™ System	$234	12.3
	SNCR/OFA/CI/LSFO	$207	14.0

SCR = Selective Catalytic Reduction (NOx)
LSFO = limestone forced oxidation FGD
CI = carbon injection (Hg)

SNCR = Selective Non-catalytic Reduction
OFA = Over Fire Air
SD/FF = Spray Dryer Fabric Filter

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Review

Status of trace element emission in a coal combustion process: a review

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Abstract

Several important aspects are described in this paper. The occurrences of trace elements (TEs) in coal are introduced. Four main groups of trace element content level, say, >50, 10–50, 1–10 and < 1 ppm, can be drawn. Trace elements partitioning in emission streams; enrichment in submicron particles; vaporization and emission in flue gas; and the mobility and leaching behavior of trace elements in coal and combustion waste are summarized. The mechanisms of trace element transformation during combustion are illustrated as following: the vaporized metals at high temperature near the combustion flame will subsequently nucleate or condense at a lower temperature downstream. These metals form a suspended aerosol along with particles. The conversion of vaporized components into various solid and/or liquid forms is the key factor influencing the final trace elements' transformation/partitioning behavior. Finally, current trace element emission control technologies are briefly introduced. To control trace elements in particle phase, electrostatic precipitators and fabric filters are mainly used. To control trace elements in vapor phase, spray dryer absorbers, wet scrubbers, condensing wet scrubbers, wet scrubbers and solid sorbent injection should mainly be used. Research needs are identified and potentially promising research topics on trace elements emission are proposed as following: (1) trace element speciation and enrichment in coal and coal ash. (2) Trace elements partitioning in combustion

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process. (3) Mechanisms of transformation and control technologies for easily vaporized TEs during combustion.

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Keywords: Trace elements; Coal combustion; Trace element emission

1. Introduction

In the future, coal will keep its important position as a world energy source because of its relatively abundant reserves in comparison to the decreasing reserves of both petroleum and natural gas. Moreover, the pollutant emissions from coal utilization may cause serious environmental and health risks, so it becomes an important issue with respect to environment protection.

The emissions of SO_x, NO_x, CO_2 and volatile organic compounds (VOC) in flue gases from coal combustion may have serious environmental impacts, such as ozone exposure at ground-level, soil acidification and euthrophication due to the deposition of acid and nitrogen, respectively, global temperature rising and direct hazards of VOC to agriculture, soil and water, etc. In comparison to the above-mentioned pollutants, the concern about the fate of trace elements (TEs) during coal combustion (i.e. partitioning, environmental impacts, emission control, etc.) is a relatively new subject.

A so-called trace element (TE) is defined as an element occurring in a very low amount (< 100 ppmw). Recently, the topic about trace elements has drawn more and more interest from scientists because of the great concern for their toxicological and environmental effects. Heavy metal is another more common term for these elements having impacts on the ecosystem and human health. This term was adopted first since at the beginning the concerned elements were all heavy metals. By now, some light elements have also been found to have great impacts on the environment (such as B, Be, As). In this study, the term trace element is chosen to represent all considered low-content elements in order to avoid the possible confusion.

The demands for studying TE behavior in flue gases from coal combustion are critical due to the following several facts [1]:

(1) Coal, as an important world energy component, will be continuously and widely used in this century due to its relatively abundant reserves;
(2) Some TEs emitted during coal combustion have great impacts on the environment and therefore on our health;
(3) The current environmental regulations address TE emission from hazardous waste incineration (HWI) and municipal waste incineration (MWI), and with no doubt more stringent limits will be proposed in the near future dealing with other combustion processes, e.g. coal combustion.

Although TE behavior from coal combustion is a relatively new subject, many studies have been developed in the last decades. In this study, a literature review with respect to TE occurrence in coal, TE emission in gases, fly ashes and bottom ashes, TE behavior in the combustion zone and finally the current studies on TE emission control.

2. Behavior of trace elements during coal combustion

2.1. Occurrences of trace elements in coal

Practically all the elements of the Chemical Periodic Table are present in coal [2–4]. According to their different contents, these elements can be divided into three groups: (1) major elements (C, H, O, N, S), whose amounts are above 1000 ppm; (2) minor elements, which include coal mineral matters (Si, Al, Ca, Mg, K, Na, Fe, Mn, Ti) and halogens (F, Cl, Br, I), present in concentrations between 100 and 1000 ppm; and (3) trace elements, which are the constituents with concentration below 100 ppm.

After numerous studies (for example, Refs. [2–18]) carried out on the occurrence and distribution of trace elements in coal, it is accepted that the TEs' combination and contents differ from one coal to another due to the different coalification processes. However, knowledge of TE distribution in coal is very important since it permits the possible prediction of TE release from combustion.

Table 1 lists the mean values of 38 TE contents in the USA, British and Australian coals based on many investigations concerning more than 1500 coal samples [2–4]. Although the TE contents seem to vary strongly with coal type, four main groups of content level can be drawn, and we can see that most TEs are less concentrated than 50 ppm.

Table 1 also tabulates the concentrations of 10 TE contents in seven Chinese coals [19–21], say, Qingshan bituminous coal in Hubei province, Heshan bituminous coal in Guangxi province, Laiyang anthracite in Shandong province, Jiafu anthracite in Fujian province, Henan lean coal, Huangshi lean coal in Hubei province and Shaoguan lean in Guangdong province.

TE release from coal combustion is affected, to a great extent, by TE occurrence modes in coal, i.e. their chemical affinities. The elements associated mostly with the coal organic and sulfide fractions tend to vaporize firstly, and then they are easily adsorbed on fine particles during flue gas cooling. In contrast, elements combined with the discrete mineral matters more possibly remain in the ash matrix. Querol et al. [6] gave an overall comparison about their results concerning the TE combinations in a Spanish coal with those obtained previously from worldwide coals before 1992 (see Table 2). Several newer reports are added at the end of this table. It can be seen that Be, Sr and Ge have an organic affinity in most reports listed in Table 2, whereas Ba, Ce, Co, La, Mn, Ni, Rb and Zr have an inorganic affinity and other TEs behave variously depending on the studies. Indeed, both TE contents and combinations in coal vary significantly with coal type.

In a more recent report, Querol et al. [12] developed an extensive study on TE distribution in both coals and wastes, and they found the following general information concerning the TE detailed combinations in coal.

Table 1

Concentrations of TEs in the US, British, Australian [2–4] and Chinese coals [19–21]—arithmetic mean values, ppm

Element and chemical symbol	Coals													
	US		British			Australian	Chinese							For most coals
	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)	(12)	(13)	
>50 ppm														
Barium (Ba)		150	70–300		142	70–300								20–1000
Boron (B)	102	50	30–60			30–60								5–400
Fluorine (F)	61	74	150		114	150								20–500
Manganese (Mn)	49	100	130		84	130								5–300
Phosphorus (P)	71		–			–								10–3000
Strontium (Sr)	37	100	100			100								15–500
Titanium (Ti)	700	800	900	63		900								10–2000
Zinc (Zn)	272	39	25			25								5–300
10–50 ppm														
Arsenic (As)	14	15	1.5		18	1.5	14.5	9.9	12.1	21.0	11.0	9.6	13.9	0.5–80
Cerium (Ce)	11		–			–								–
Bromine (Br)	15		–			–								–
Chlorine (Cl)			150			150								50–2000
Chromium (Cr)	14	15	6		34	6	36.8	25.4	21.6	30.4	26.0	12.0	74.0	0.5–60
Copper (Cu)	15	19	15	48		15	27.5	33.4	31.4	21.6	23.3	19.5	32.1	0.5–50
Lead (Pb)	35	16	10	48	38	10	20.9	18.1	12.2	29.4	22.8	22.7	24.4	2–80
Lithium (Li)		20	20			20								1–80
Nickel (Ni)	21	15	15		28	15	13.9	18.6	17.1	17.0	12.4	9.3	24.9	0.5–50
Rubidium (Rb)	14													2–50

Vanadium (V)	33	20	20		76	20	76.5	100.0	70.8	54.2	48.5	38.3	109.0	2–100
Zirconium (Zr)	72	30	100			100								5–200
1–10 ppm														
Antimony (Sb)	1.3	1.1	0.5		3.1	0.5								0.05–10
Beryllium (Be)	1.6	2	1.5		1.8	1.5	3.1	2.6	1.8	1.3	1.9	1.3	2.5	0.1–15
Cadmium (Cd)	2.5	1.3	0.08	0.24	0.4	0.08	0.19	0.15	0.29	0.30	0.10	0.08	0.25	0.1–3
Caesium (Cs)			1.3			1.3								0.3–5
Cobalt (Co)	9.6	7	4			4	8.5	9.5	11.6	7.4	6.7	5.6	10.8	0.5–30
Gallium (Ga)	3.1		4			4								1–20
Germanium (Ge)	6.6		6	6.8	5.1	6	1.95	1.48	0.47	0.40	0.94	0.63	0.93	0.5–50
Iodine (I)	2.0		–			–								–
Lanthanum (La)	6.9		16			16								–
Molybdenum (Mo)	7.5	3	1.5		< 2	1.5								0.1–10
Niobium (Nb)		3	–			–								1–20
Scandium (Sc)	2.4	3	4			4								1–10
Selenium (Se)	2.1	4.1	0.8		2.8	0.8								0.2–4
Thallium (Tl)			–			–								< 0.2–1
Thorium (Th)	2.0		2.7	3.9		2.7								0.5–10
Uranium (U)	1.6	1.8	2		1.3	2								0.5–10
< 1 ppm														
Mercury (Hg)	0.2	0.18	0.1	0.2		0.1								0.02–1
Silver (Ag)	0.2		< 0.1			< 0.1								0.02–2
Tantalum (Ta)	0.15													

(1) 101 samples of mainly Illinois bituminous coals; (2) 799 samples of bituminous and sub-bituminous coals; (3) 23 samples of bituminous coals; (4) 231 samples of bituminous coals; (5) number of samples not stated, bituminous coals; (6) 452 samples of New South Wales bituminous coals; (7) Qingshan bituminous coal; (8) Heshan bituminous coal; (9) Laiyang anthracite; (10) Jiafu anthracite; (11) Henan lean coal; (12) Huangshi lean coal; (13) Shaoguan lean coal.

Table 2
Classification of trace elements in coals as a function of the inorganic, organic or intermediate affinities [6][a]

Authors	Affinity		
	Inorganic	Organic	Intermediate
Minchev and Eskenazy (1972)	Be, Sc, Zr, Ti, Cr	Ge, As, Ag, Y, Mo, Yb, Sr, Ba, V, Mn, Cu, Ni, Sn, Zn, Co	
Gluskoter et al. (1977)	Zn, Cd, Mn, As, Mo, Fe	Ge, Be, B, Sb, Cr, Se	Co, Ni, Cu
Miller and Given (1978)		B, Be, Ge, Na, P, Mg, Cl, Br	
Kuhn et al. (1980)	As, Cd, Zn	B, Be, Br, Ge, Sb	Ga, Ni, P, Ti
Ward (1980)	Cu, Pb, Zn, Mn, Sr, Cr	B, Ni, V, Zr, Co, Be	Ge
Azambuja et al. (1981)	Mn, Zn, Pb	Cu, Co, Ni, Cr, V	
Harvey et al. (1983)	As, Ba, Cd, Mn, Mo, Pb, Tl, Zn	B, Be, Br, Ge, Ni, Sb, U, V	
Correa et al. (1984)	Ga	B, V, Cr	
Karner et al. (1986)	Sr, Ba		
Kojima and Furusawa (1986)	Mn	Ti, V, Sr, B	Ba, Sn, Cr, Ni, Sc, Y, Be, Co, Cu, Zn, Zr, As
Kortenski (1986)	Mn, Zn, Bi, Sn, Sr, Tl	Ag, As, Ge, Mo, Ni, W, Ba, Co, Cr, Cu, Pb, Ti, V, Zr	
Warbrooke et al. (1986)		Ge, Mo, Ni, Be, Br	
Goodarzi (1987)		As, B, Br, Cl	
Goodarzi et al. (1987)	Ti, Cr, Hf, Ta, Th, V	Br, Mn, Cl	
Miller and Given (1987)	Ce, Zr, Pb, Zn	Cu, Be, Y, Yb, V, Ge, Ti, Ni, Ga, Sr, Ba, Mn	
Rimmer (1991)	Ba, Mn, Rb, Sr, Zn, Zr	Be, Ni	Cu, V
Beaton et al. (1991)	Ti, Sb, As, Be, Cs, Li, Ni, Pb, V, Zn, Rb, Mn	Sr, B, Br	As, Ba, Co, Mo, Ce, Dy, Lu, Sc, W, U
Pires et al. (1992) [8]	Co, Mn, Ni, V		As, Cd, Cr, Cu, Mo, Zn
Querol et al. (1992) [6]	Ba, Ce, Cr, Rb, Co, Ni	Be	As, Cd, Cu, Dy, Er, Eu, Gd, Ge, Ho, Lu, Mo, Nd, Pb, Pr, Sm, Sb, Sr, Tb, Th, Tm, U, Yb, Zn
Martinez-Tarazona et al. (1992) [7]	Cu, Ni, Zn, Pb	Mn, Zr, Nb	Rb, Ba, Cr, Sr, V, Y
Spears et al. (1993) [9]	Pb, Cu, Ni, Zn, Mn	V, Sr, Ba, Zr, Nb	
Mercer et al. (1993) [10]	Mn, Fe	V	As, Co, Mo, Ni, Sb, Se, Zn
Querol et al. (1995) [12]	Al, K, Mg, Na, P, Ti, Li, Cr, Ni, Cu, Ga, Rb, Sr, Y, Sn, Cs, Ba, Ta, Pb, Bi, Th, U, REEs, Fe, Co, Zn, As, Se, Mo, Cd, Sb, Hg, Tl, Ca, Mn, Co	Be, Ge, Zr	C, N, S, B, V, W
Lu et al. (1995) [13]	As, Co, Cr, Cu, Ni, Pb, V	Be, Ge	

[a] Unreferenced authors can be found in Ref. [6].

(1) Elements showing inorganic affinity in coal

In clay minerals and feldspars: Al, Ba, Bi, Cr, Cs, Cu, Ga, K, Li, Mg, Na, Ni, P, Pb, Rb, Sn, Sr, Ta, Th, Ti, U, V, Y and REES (rare earth elements).
In iron sulfides: As, Cd, Co, Cu, Fe, Hg, Mo, Ni, Pb S, Sb, Se, Ti, W and Zn.
In carbonates: C, Ca, Co and Mn.
In sulfates: Ba, Ca, Fe and S.
In heavy minerals (tourmaline): B.
In several mineral phases: Co and W (carbonates and sulfides); Ni, Cu, Pb (clay minerals and sulfides); S (sulfides, sulfates and organic matter); C (carbonates and organic matter).

(2) Elements showing organic affinity in coal.

C, N, S, Be, B, Ge, V, W and Zr (boron exhibits partial association with tourmaline in the heavy fraction, and V with clay minerals).

To conclude, both TE concentration and their chemical affinity vary strongly with the considered coals. The comparison between results concerning studies about worldwide coals is useful to find out some general rules. However, it still needs a long time to achieve a great step forward in the research dealing with TE combinations in coal. This part of work is paramount, especially when one is interested in TE partitioning in the coal-fired flue gases.

2.2. Emissions of trace elements in gases and ashes

Many papers, including several reviews [22–27], have reported TE emission from coal combustion with respect to the following aspects: the TE size-distribution in fly ashes and their enrichment in the submicron particles [12,23,28–38], the formation and transformation of fly ash particles [39–44], the direct gaseous emission of several volatile TEs, i.e. halogens, B, Hg, Se and As, etc. [45–56], the mobility and leaching behavior of TEs in coal and combustion waste [11,57–64]. Moreover, several overviews dealing with TE emission from HWI and MWI are also presented [65–69].

2.3. Trace element partitioning in emission streams

The TEs introduced into a combustion system as part of the coal feeds or sorbents can only exit the combustion system through a finite number of pathways. In this study, TE partitioning is often referred to the dispersion of elements among different emission streams: bottom ash, fly ash, ash in scrubber waste and flue gas.

Fig. 1 illustrates the partitioning of various TEs (i.e. the fraction of the total elemental mass input that is discharged from the combustion system via each emission stream) from a pulverized coal-fired boiler located in the Netherlands [22]. Notice that the main proportion of almost all elements is bound with the fly ash and collected in the electrostatic precipitator (ESP). Boron (B) and selenium (Se) are partially discharged in the vapor phase, and mercury (Hg), which exhibits a very high vapor pressure at typical stack outlet temperature, is almost fully released with the flue gas.

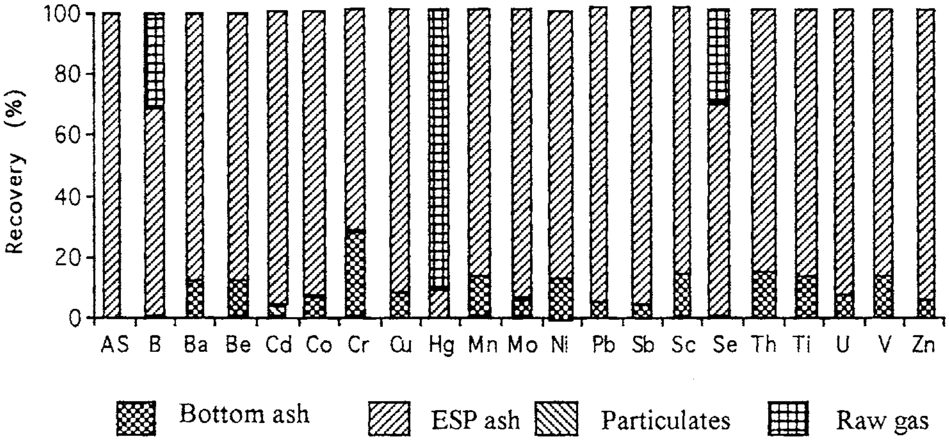

Fig. 1. Relative distribution of trace elements between bottom ash, ESP ash, particulate emission and the raw gas based on data from a coal-fired power station in Netherlands [22].

2.4. Trace element enrichment in submicron particles

The TE enrichment trends in submicron particles have been reported by many authors [12,28–39]. Most TEs, which are partially or fully vaporized during coal combustion, tend to condense and enrich in the submicron particles with a significant surface-to-volume ratio. The submicron particles have more harmful impacts than the supermicron particles since they have long residence time in the atmosphere and a high probability to deposit in human being lungs. Moreover, they can be collected by air pollution control devices (APC) with very low efficiency only.

A typical aspect of the particle bimodal distribution has been presented by Linak and Wendt [23]. It is found that although the fraction of submicron fly ash before APC contains less than 5% of the total mass, it represents approximately 50% of the total mass after it. Based on partition and enrichment behavior of elements, three basic classes of trace elements can be defined:

Class I: Elements approximately equally distributed between the bottom ash and fly ash, or show no significant enrichment or depletion in the bottom ash.
Class II: Elements enriched in the fly ash and depleted in the bottom ash, or show increasing enrichment with decreasing fly ash particle size.
Class III: Elements totally emitted in the vapor phase.

Linak and Wendt [23] summarized previous studies on TE size distribution in particles and the results are listed in Table 3. It can be seen clearly that most regulation-concerned TEs are enriched in submicron particles, and hence they have more risks of environmental and health impacts.

2.5. Trace element vaporization and partitioning

The most volatile TEs (Hg, Se, As), to which we have often paid more attention, and halogens, etc., remain mostly in the vapor phase as they pass through heat transfer

Table 3
Coal combustion investigations describing TE enrichment in submicron fly ash [23]

Investigation	Submicron enriched	No enrichment trend	Submicron depleted
Davison et al. (1974)	Sb, As, Cd, Cr, Pb, Ni, Se, S, Tl, Zn	Al, Be, C, Fe, Mg, Mn, Si, V	Bi, Ca, Co, Cu, K, Sn, Ti
Kaakinen et al. (1975)	Sb, As, Cu, Pb, Mo, Po, Se, Zn	Al, Fe, Nb, Rb, Sr, Y	
Klein et al. (1975)[d]	Sb, As, Cd, Cu, Cr, Ga, Pb, Mo, Ni, Se, Na, U, V, Zn	Al, Ba, Ca, Ce, Co, Eu, Hf, Fe, La, Mg, Mn, K, Rb, Sc, Si, Sm, Sr, Ta, Th, Ti	
Gladney et al. (1976)	Sb, As, Br, I, Pb, Hg, Se	Na	Ce, Fe
Coles et al. (1978)	Pb, Ra, Th, U	Ce	
Ondov et al. (1978)	Sb, As, Ba, Ga, In, Mo, Se, U, V, W, Zn		
Desrosiers et al. (1979)	Si, S	Ca, Mg, K, Na	Al, Fe
Ondov et al. (1979)	Sb, As, Ba, Mo, Se, V, W		
Smith et al. (1979)	Sb, As, Br, Cu, Cr, Ga, Pb, Hg, Mo, Ni, Se, S, Sn, V, Zn	Fe, Mg	
Smith et al. (1980)[e]	As, Cu, Cr, Ga, Ge, Pb, Mo, Ni, Se, Sn, V, Zn	Al, Ba, Ca, Ce, Fe, La, Mn, Nb, K, Rb, Si, Sr, Ti, Y, Zr	
Markowski et al. (1980)	Sb, As, Cd, Cr, Ni, Rb, Se, V, Zn	Fe, Ti	Al, Hf, Mg, Mn, Ta
Biermann and Ondov (1980)	Ba, Se, U, W	Fe, Na	
Flagan et al. (1981)	C, Si, Na, S		
Damle et al. (1982)[a]	Sb, As, Cd, Pb, Mo, Se, W, Zn	Ba, Cr, Co, Ni, Mn, Na, Sr, V[b]	Al, Ca, Ce, Hf, Fe, Mg, K, Si, Ti[c]
Neville and Sarofim (1982)	Al, Sb, As, Si, Na	Fe, Mg	
Quann et al. (1982)	Mg, K, Na		
Quann et al. (1982)	Sb, As, Cr, Cl, Co, Mg, P, K, Na, Zn		Al, Sc, Th
Haynes et al. (1982)	Sb, As, Fe, Mn, Hg, K	Mg	Al, Ca, Si
Shendrikar et al. (1983)	Sb, As, Cl, Hg, Ni, Se, Zn		Al, Ca, Mg
Neville et al. (1983)	Al, Sb, As, Cr, Na, Zn	Ca, Fe, Mg	
Linak et al. (1986)	As, Pb, K, Na, Zn	Al, Ca, Fe, Mg, Mn, Si, Ti	
Kauppinen and Pakkanen (1990)	Ca, Cd, Cu, Pb, Sr, S, V	Al, Fe, Mg, Mn, Na, Si, Ti, Zn	

a: literature review, b: slight enrichment or no change, c: no change or slight depletion, d: species Br, Cl, Hg, Se in vapor phase, high filter penetration, e: species As, Br, Cl, I, Hg, Se in vapor phase, high filter penetration.

sections of a boiler. The percentages of the total in-stack concentrations of these elements in the vapor phase have been reported [22] to be: Cl, up to 99% as HCl; F, up to 90% as HF; Br, 25–98% as HBr; Hg, up to 98% as Hg, HgO and CH_3Hg; Se, up to 59% as Se and SeO_2; As, 0.7–52% as As_2O_3; and I, 90–99% as HI. Although mercury (Hg) concentration in coal is usually extremely low, significant attention is focused on its emission because its capture by APC systems is problematic, and moreover, it is highly toxic to human health and it bioaccumulates. Many studies dealing with the behavior of most volatile elements and their gaseous emission exist in the literature [45–56].

Actually, TE vaporization behavior is closely related to their partitioning in emission streams and their different enrichment phenomena. The TE classification into three groups, based on the TE enrichment behavior in submicron particles, was mentioned before [22]. Fig. 2 correlates the TE class behavior with the measure of volatility (e.g. boiling point), and it indicates the potential for intermediate behavior.

Fig. 2 points out the following facts:

(i) The elements (minor and trace) not vaporized during combustion will compose the matrix of both fly ash and bottom ash in the form of a homogeneous 'melt' as well as crystalline phases.

(ii) The elements partially or fully vaporized will undergo additional transformations and partitioning downstream, as the flue gas cools down in the upper furnace and heat recovery section of the combustion system. The TE conversions are decided into three complex and interrelated processes: adsorption, condensation and chemical transformation.

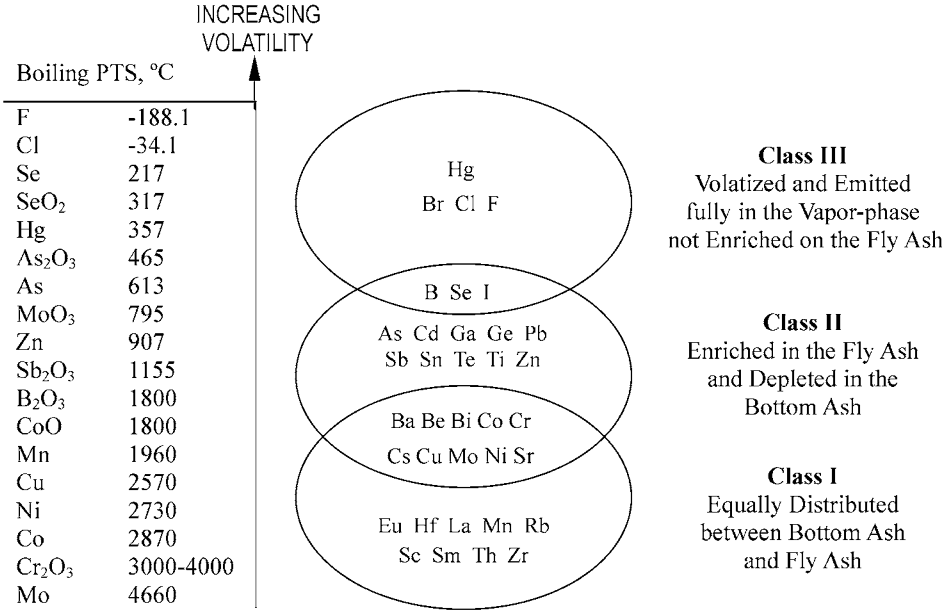
INCREASING VOLATILITY
Boiling PTS, °C
F -188.1
Cl -34.1
Se 217
SeO2 317
Hg 357
As2O3 465
As 613
MoO3 795
Zn 907
Sb2O3 1155
B2O3 1800
CoO 1800
Mn 1960
Cu 2570
Ni 2730
Co 2870
Cr2O3 3000-4000
Mo 4660
Hg
Br Cl F
B Se I
As Cd Ga Ge Pb
Sb Sn Te Ti Zn
Ba Be Bi Co Cr
Cs Cu Mo Ni Sr
Eu Hf La Mn Rb
Sc Sm Th Zr
Class III
Volatized and Emitted fully in the Vapor-phase not Enriched on the Fly Ash
Class II
Enriched in the Fly Ash and Depleted in the Bottom Ash
Class I
Equally Distributed between Bottom Ash and Fly Ash

Fig. 2. Categorization of trace elements based on volatility behavior [22].

2.6. Mechanisms of trace element transformation during combustion

The vaporized metals at high temperature near the combustion flame will subsequently nucleate or condense at a lower temperature downstream. These metals form a suspended aerosol along with particles which are generated by other mechanisms [39–44]. Both experimental and model studies have been developed on TE vaporization [24,70–76], aerosol dynamics [28,77–83] and TE transformation routes in the combustion zone [23].

2.7. Trace element transformation mechanism overview

Once combustion gases are away from the combustion zone of a coal-fired boiler, the key factor influencing the final trace element transformation/partitioning behavior is the conversion of vaporized components into various solid and/or liquid forms. It is determined, basically, by three complex and interrelated processes: adsorption, condensation and chemical transformation.

Fig. 3 shows possible ways along which TEs are partitioned into vapor, submicron aerosol and supermicron aerosol. Several paths which pertain specifically to coal are distinguished by thick bold arrows and lines.

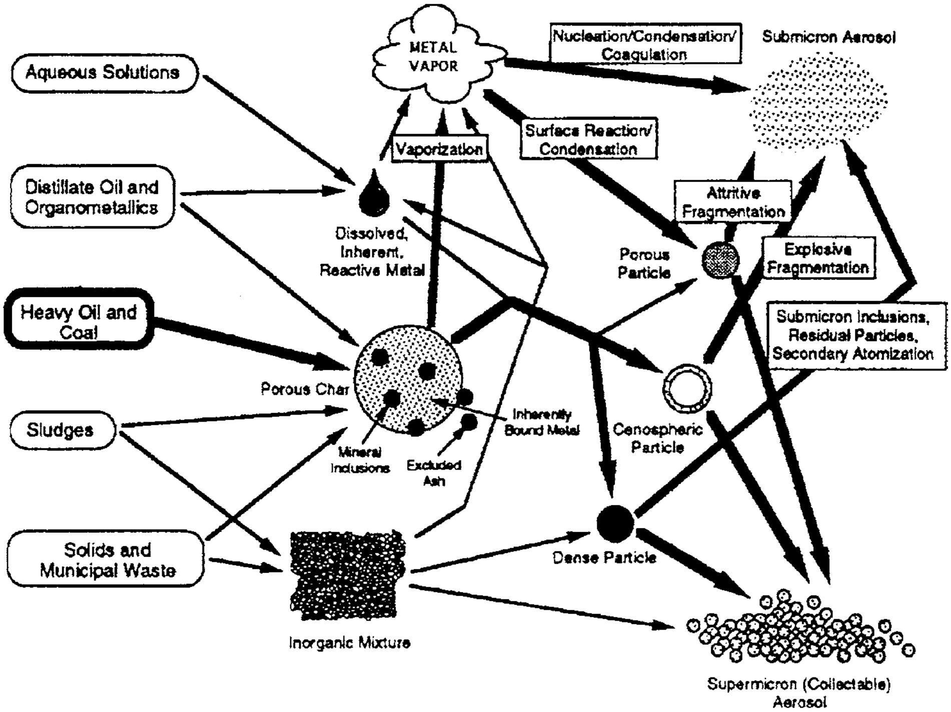
METAL VAPOR
Nucleation/Condensation/ Coagulation
Submicron Aerosol
Aqueous Solutions
Vaporization
Surface Reaction/ Condensation
Distillate Oil and Organometallics
Attritive Fragmentation
Dissolved, Inherent, Reactive Metal
Porous Particle
Explosive Fragmentation
Heavy Oil and Coal
Submicron Inclusions, Residual Particles, Secondary Atomization
Porous Char
Inherently Bound Metal
Sludges
Cenospheric Particle
Mineral Inclusions
Excluded Ash
Solids and Municipal Waste
Dense Particle
Inorganic Mixture
Supermicron (Collectable) Aerosol

Fig. 3. The mechanisms for particle formation in a combustion system [23].

The involved physico-chemical phenomena [22] which control TE partitioning and their final physical form are as follows:

(i) Heterogeneous condensation on the existing fly ash particles and heat exchange surfaces.
(ii) Physical/chemical adsorption on fly ash particles.
(iii) Homogeneous condensation (nucleation) and coalescence as submicron aerosols if local supersaturation condition exists.
(iv) Homogeneous and heterogeneous chemical reaction among trace elements, fly ash and flue gas constituents.
(v) Remaining in the vapor phase for species with high vapor pressure at typical boiler exit temperature.

In addition, the metal aerosol dynamics is the theoretical base deciding fly ash formation and particle size distribution (PSD).

2.8. Metal vaporization kinetics

The real TE combination in coke is quite complex, and therefore, their vaporization during coal combustion depends greatly on their speciation in the coke, in addition to the combustion conditions. Several TE vaporization mechanisms are displayed in the following equations:

$$\text{Chlorides: } \mathrm{MCl}_x(\mathrm{cr}) \Leftrightarrow \mathrm{MCl}_x(\mathrm{g}) \tag{1}$$

$$\text{Sulphides: } \mathrm{MS}_y(\mathrm{cr}) \Leftrightarrow \mathrm{MS}_y(\mathrm{g}) \tag{2}$$

$$\text{Oxides: } \mathrm{MO}_z(\mathrm{cr}) + \mathrm{CO(g)} \Leftrightarrow \mathrm{MO}_{z-1}(\mathrm{cr}) + \mathrm{CO_2(g)} \tag{3}$$

$$\mathrm{MO}_{z-1}(\mathrm{cr}) \Leftrightarrow \mathrm{MO}_{z-1}(\mathrm{g}) \tag{4}$$

In Eq. (1), MO_{z-1} is the sub-oxide or elemental form of a metal (M) normally more easily vaporized than the oxide form (MO_z); moreover, the metal oxide can be formed at relatively high temperature by other metallic compounds in coal:

$$\mathrm{MAO}_w(\mathrm{cr}) \Leftrightarrow \mathrm{MO}_z(\mathrm{cr}) + \mathrm{AO}_{w-x}(\mathrm{g}) \text{ or } (\mathrm{cr}) \tag{5}$$

Where A represents coal major and minor elements i.e. C, N, S, Si, Al, P, Ti, Mn, etc.

Quann and Sarofim [70] claimed that Eq. (1) is the classical mechanism (reducing mechanism) for the vaporization of refractory metal oxides contained in coal, whereas Baxter et al. [71] recently found that Fe constituents in coal are vaporized according to an oxidizing mechanism. Moreover, the rapid vaporization of TEs chlorides and sulfides may occur before or during the first period of coal combustion.

Ho et al. [73] had ever proposed a metal volatilization sub-model describing the metal vapor diffusion through a clay particle during the fluidized bed thermal treatment of metal-containing clay soil.

2.9. Modeling of trace elements speciation during combustion

Up to now, most work on the mechanism of trace element speciation has been focused on mercury, while a few studies were on chromium [48,84–95]. Previous studies of mercury oxidation in combustion systems have been focused on chemical equilibrium calculation and experimental measurements. Equilibrium calculations conducted for mercury at stack gas conditions indicate that it is the oxidized form that is thermodynamically favored. However, of the two possible oxidized forms, there appears to be little experimental evidence for the existence of mercurous compounds in coal combustion flue gases [84]. Mercury speciation in post-combustion conditions thus requires an understanding of the partitioning between elemental Hg (0) and Hg (+2) oxidation states only.

It is well recognized that under actual combustion conditions, Hg oxidation would be subject to kinetic control. Hall et al. [48,85] and Widmer and West [86] proposed one-step global reaction mechanisms to model the observed depletion of Hg^0 in the presence of Cl_2 or HCl. While such mechanisms can give plausible qualitative results, they are generally not suited for examining the effects of other flue gas constituents, e.g. NO_x, H_2O and SO_2 on Hg chlorination. Furthermore, such mechanisms provide little insight into the details of the conversion process. Recently, marked strides have been made in unraveling the reaction mechanism for homogeneous Hg oxidation through a sequence of elementary reactions. Such efforts include those of Senior et al. [87], Sliger et al. [88], Edwards et al. [89] and Niksa et al. [90]. Of those efforts, Ref. [89] provides the most complete Hg chlorination pathways to date as well as a pathway involving HgO, with model predictions in good accord with experimental data for higher reactor temperatures but a drastic underprediction of Hg chlorination for lower temperatures. Ref. [90] developed and evaluated an elementary reaction mechanism for homogeneous Hg^0 oxidation with emphasis on major interactions among Cl species and other pollutants in coal-derived exhausts. Their model predictions showed that Hg oxidation is primarily through a Cl atom recycle process, with Cl and Cl_2 concentrations both playing an important role. O_2 weakly promotes homogeneous Hg oxidation, whereas moisture is a stronger inhibitor. NO can promote or inhibit homogeneous Hg oxidation, depending on its concentration. Ref. [91] proposed an important and previously unrecognized pathway of homogeneous Hg oxidation mechanism including Hg reactions involving HgO, in which the reaction rate constants were calculated neither from experimental data nor by estimated but directly from transition state theory. A relatively complete homogeneous mercury oxidation mechanism including reactions of mercury chlorination and oxidation is tabulated in Table 4, where the rate coefficients are in the modified Arrhenius form

$$k = AT^{\beta}\exp(-E_a/RT)$$

The activation energy E_a, the temperature exponent β and the pre-exponential constants A are parameters in the model formulation.

Table 4
Kinetics and rate constants in Hg^0 oxidation mechanism

No.	Reactions	A (cm^3/mol – s)	β	E_a (kcal/mol)	Reference
1	$Hg + Cl + M = HgCl + M$	2.4e8	1.4	– 14.4	Widmer et al. [86]
2	$Hg + Cl_2 = HgCl + Cl$	1.39e14	0.0	34.0	Widmer et al. [86]
3	$HgCl + Cl_2 = HgCl_2 + Cl$	1.39e14	0.0	1.0	Widmer et al. [86]
4	$HgCl + Cl + M = HgCl_2 + M$	2.19e18	0.0	3.10	Widmer et al. [86]
5	$Hg + HOCl = HgCl + OH$	4.27e13	0.0	19.0	Widmer et al. [86]
6	$Hg + HCl = HgCl + H$	4.94e14	0.0	79.3	Widmer et al. [86]
7	$HgCl + HCl = HgCl_2 + H$	4.94e14	0.0	21.5	Widmer et al. [86]
8	$HgCl + HOCl = HgCl_2 + OH$	4.27e13	0.0	1.0	Widmer et al. [86]
9	$Hg + ClO = HgO + Cl$	1.38e12	0	832	Xu et al. [91]
10	$Hg + ClO_2 = HgO + ClO$	1.87e7	0	51.27	Xu et al. [91]
11	$Hg + O_3 = HgO + O_2$	7.02e14	0	42.19	Xu et al. [91]
12	$Hg + N_2O = HgO + N_2$	5.08e10	0	59.81	Xu et al. [91]
13	$HgO + HCl = HgCl + OH$	9.63e4	0	8.92	Xu et al. [91]
14	$HgO + HOCl = HgCl + HO_2$	4.11e13	0	60.47	Xu et al. [91]

2.10. Current trace element emission control technologies

2.10.1. General information

The final objective of all studies concerning TE behavior from coal combustion is to reduce their emission levels while keeping high coal combustion efficiency. Many publications report studies on TE emission control [96–110], most of them concern the municipal and hazardous waste incineration since it may induce the release of constituents contained in these waste streams, including many toxic metals. Nevertheless, many of the control technologies concerning TE emissions from HWI and MWI can be subsequently applied to coal combustion systems since processes are rather similar.

Donnelly [101] reported a review about metal emission control technologies for waste incineration. The major fraction of toxic metals found in flue gases exists as fine-particle matter; nevertheless, a significant fraction of certain metals (such as B, Hg, Se) exists in the vapor phase at typical incinerator (or boiler) exit flue gas conditions. The control of the particulate fraction is achieved by utilizing traditional particulate control devices. That of the vapor phase fraction is achieved through cooling of the flue gas and collection of the fine particulate thus formed. Table 5 lists the types of control typically employed to reduce toxic metals emission. In the next sections, we give more details about the control methods of toxic metals.

2.10.2. Spray dryer absorption systems

Spray dryer absorption (SDA) has been widely applied for waste incinerator emission control, and it has demonstrated high collection efficiencies for most toxic metals present in the flue gas. SDA has been specified as the best available control technology in a number of municipal waste incinerator air permits.

A typical SDA process includes a reagent preparation system, a spray dryer absorber and a dust collector. Flue gas enters the spray dryer, where it is contacted by a cloud of finely atomized droplets of reagent (typically hydrated lime slurry). The flue gas

Table 5
Toxic metal controls [100]

Fraction	Control device
Metals in particle	Electrostatic precipitators Fabric filters Wet scrubbers
Metals in vapor phase	Spray dryer absorbers Wet scrubbers Condensing wet scrubbers

temperature decreases and the humidity increases as the reagent slurry simultaneously reacts with acid gases and evaporates to dryness. In some systems, a portion of the dried products is removed from the bottom of the spray dryer, whereas in others, it is carried over to the dust collector. Collected reaction products are sometimes recycled to the feed system in order to reduce reagent consumption.

Toxic metal removal in the dust collector is enhanced by cooling the incoming flue gas (from 2000 to 450 °C) as it passes through the spray dryer. Because of the cooling, some vaporized metals condense to form fine particulates, which grow through impaction and agglomeration with the very high number of lime droplets produced by atomization devices. Then these agglomerated particles are easily removed. Generally, the lower the spray dryer outlet temperature, the higher the efficiency of the acid gas absorption and the vaporized toxic metal removal. The minimum reliable operating outlet temperature depends on the spray dryer and dust collector design, and on the composition of the dry fly ash reaction product. The spray dryer outlet temperature must be maintained high enough to ensure complete reagent evaporation and the production of a free-flowing product.

2.10.3. Wet scrubbers

Wet scrubbers control the vapor phase emissions through gas cooling and collection of the resulting condensed fine toxic metal particulates. The most commonly used wet scrubbers for this type of service are the electrostatically (or ionizing) enhanced wet scrubbers and the condensing wet scrubber.

Electrostatically enhanced scrubbers capture the condensed fine particulate by imparting a charge to the incoming particulate and then collecting these charged particles on neutral packing material or negatively charged collecting electrodes.

Condensing wet scrubbers sub-cool the incoming flue gas to below its adiabatic saturation temperature. This will cause the condensation of a larger fraction of the vapor phase metals, and in addition, it induces water vapor to condense forming a large number of droplets to aid in the collection of fine toxic metal particulate.

In this system, the flue gas enters the quenching section where it is first cooled to its saturation temperature. Then it goes to the condenser/absorber where it is further cooled to about 10–90 °F by contact with a cooled reagent stream. Afterwards, the flue gas (now containing condensed toxic metal particulate and water droplets) passes through the collision scrubber, where the fine droplets impinge on a flat surface. There the fine particulate and water droplets interact and agglomerate, resulting in particulate capture.

Finally, the flue gas passes through an entrainment separator for droplet removal and it is discharged through the stack.

2.10.4. Sorbent injection

It should be noticed that the high volatility and existence in the vapor phase make such trace element control a very difficult task to accomplish. In principle, trace elements in vapor phase can be condensed by lowering the temperature. However, as indicated above, the resulting loss in buoyancy of the flue gas would require reheating the flue gas, which would not be economical. Furthermore, the resultant particles may be in the submicrometer sizes, and these particles are not effectively captured in conventional particulate control devices [111]. Capture of these species on sorbents by physical or chemical means is therefore a very attractive alternative.

Various researchers have studied the interaction between trace metals and various sorbents [112]. The sorbent–metal interaction can be physical or chemical in nature, or it can be a combination of these two processes depending on the temperature under consideration. Prior investigations have been conducted to determine the effectiveness of different mineral sorbents in the removal of cadmium, lead and alkali metal compounds from hot flue gas. Uberoi and Shadman [113] have studied the use of mineral sorbents such as silica, alumina, kaolinite, emathlite and lime for the removal of cadmium compounds from high temperature (800 °C) flue gases. They found the overall sorption process to be a complex combination of physical adsorption and chemical reaction. Gullett and Raghunathan [114] investigated the effectiveness of high-temperature furnace sorbent injection for capture of metal emissions on pilot scale. Mineral sorbents such as hydrated lime, limestone and kaolinite were shown to be effective for arsenic, cadmium and lead capture at 1000–1300 °C range. Ho et al. [115] reported that in a fluidized bed combustor, optimum capture of lead and cadmium using mineral sorbents takes place at around 700 °C. Other sorbents such as fly ash and activated carbon have shown to be possible alternatives to these mineral sorbents. Trace elements such as As, Cu, Mo, Pb and Zn have been shown to be concentrated on fly ash in a power station flue gas [116]. Wouterlood and Bowling [117] studied the capture of arsenious oxide (As_4O_6) on activated carbon. They found that activated carbons were quite effective in trapping the oxide, and the amount of As_4O_6 absorbed at saturation ranged from 25% to 45% of the weight of carbon at 200 °C. The capture was reversible and it increased with the total surface area of the activated carbon. Cheng et al. [110] investigated the effects of limestone, $CaSO_4$, bauxite, kaolinite and CaO on the emission of trace elements, SO_2 and NO_x during coal combustion. They found that the absorptive capacity is related to the qualities of the absorbents (type, amount and particle size) and the combustion temperature. Their results also show that some absorbents can reduce SO_2 emission simultaneously, but no influence on NO_x emission. Vassilev et al. [118] found that kaolinite and montmorillonite or coals enriched in these minerals are perspective sorbents and inertants for a retention of the most volatile Pb, Sb and Cu in refuse-derived char ash from municipal solid waste.

In the past few years, dry sorbent injection for in situ capture of metal from hot flue gas has been studied with the aim of developing a potential control technique. Due to the occurrence of multiple trace elements in flue gas in addition to SO_2, NO_x, etc.,

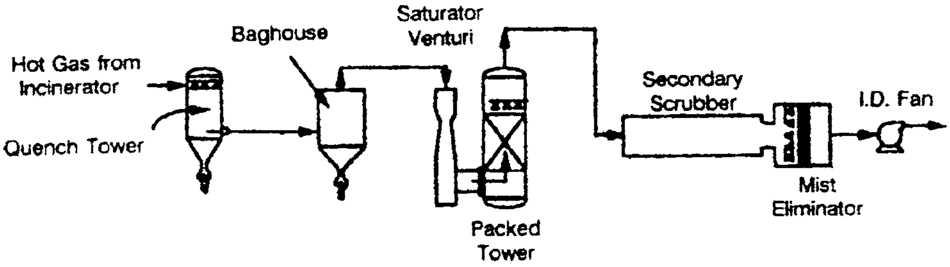

Fig. 4. Combined systems approach—emissions control scheme [100].

recent efforts of the research community have been geared towards developing a multifunctional sorbent which is capable of reducing emission of most of the pollutants below a certain acceptable standard. Activated carbon offers an attractive option for use as a multifunctional sorbent in the low temperature range because of its performance in capturing mercury and SO_2. Direct injection of activated carbon into the flue gas stream in the duct region has been proposed to be an effective technology since it has the potential for high mercury removal efficiencies. Calcium-based sorbents, because of their low cost, have been used extensively for the capture of acidic species such as sulfur dioxide. These sorbents also offer an attractive option to be used as multifunctional sorbents because of their ability to capture sulfur species as well as trace elements such as selenium and arsenic species. When used as a sorbent to capture the toxic species in the flue gas, the sorbent interacts with various components and the extent of interaction kinetics depends on the individual sorbent species. Sulfation kinetics of these sorbents has been extensively studied in the literature, however, it lacks a systematic study investigating the interaction kinetics of lime sorbents with trace metals such as arsenic.

Emissions levels of toxic metals from incinerators equipped with modern air-pollution control systems are several orders of magnitude lower than levels in 1980. High collection efficiencies are achieved for the 10 toxic metals proposed for regulation (Ag, As, Ba, Be, Cd, Cr, Hg, Pb, Sb and T1) [101]. Current regulations are based on health risk assessments, and set emission limits that are highly protective of human health and of the environment. However, continued public concern regarding incinerator metal emissions may result in additional and more complex control systems being required in the future. For example, Fig. 4 shows a combined systems approach to strongly control incinerator emissions.

3. Promising research topics on trace element emission

Based upon the literature review above, the following research aspects are promoted:

(1) Trace element speciation and enrichment in coal and coal ash.
The relationship between associated elements and coal macerals with mineral matter should be investigated by systematical tests of TE speciation and enrichment in typical

coals and their fly ash. Meanwhile, the quantitative relationship between TE partitioning in fine particulates with TE content, form and other compositions in coal should also be studied.

(2) Trace element partitioning in combustion process.
A new thermodynamic equilibrium model including equilibrium calculation of interactions between elements should be developed based upon the chemical equilibrium principle. The model can be used to predict the status of TEs in the combustion process and their partitioning following cooling process in the flue gas. Thus, the reaction mechanisms of TEs and the interaction between TEs and other pollutants in the combustion process can be obtained.

(3) Mechanisms of transformation and control technologies for easily vaporized TEs during combustion.
A relatively effective model should be developed using heterogeneous chemical kinetics to describe the transformation and mobility characteristics of easily vaporized TEs in a combustion process. The vaporization, nucleation mechanisms of TEs, their retention by fly ash and the reaction mechanisms of solid sorbents with TEs should be further investigated, with an objective to develop simultaneous control technologies for TEs and other pollutants with high efficiency and low investment.

4. Conclusion

In this study, a brief introduction is given about the environmental hazards of coal energy, and more details focused on TE toxicity and the current legislation concerning TEs. This part of introduction shows the absolute necessity of reducing pollutant emission from coal utilization due to the great concern to their environmental and health impacts and the existing (or to come) regulation limits. The TE behavior during coal combustion is reviewed, with a number of information about TE occurrences in coal; their emission in gases, fly and bottom ashes; their behavior in the combustion zone and their transformation mechanism; their kinetic oxidation mechanism; and some current technologies of TE emission control. Finally, research needs on trace element emission are discussed.

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References

[1] R. Yan, Partitioning of trace elements in the flue gas from coal combustion, PhD dissertation, Centre National de la Recherche Scientifique, Odeillo, France, 1999.
[2] D.J. Swaine, Trace Elements in Coal, (M), Butterworth, London, 1990.
[3] D.J. Swaine, F. Goodarzi, Environmental Aspects of Trace Elements in Coal, (M), Kluwer, Dordrecht, 1995.

[4] E. Raask, The mode of occurrence and concentration of trace elements in coal, Fuel 11 (1) (1985) 97–118.

[5] J.A. Solari, H. Fiedler, C.L. Schneider, Modeling of the distribution of trace elements in coal, Fuel 68 (5) (1989) 536–539.

[6] X. Querol, T.J.L. Fernandez, S.A. Lopez, M.E. Duran, Trace elements in high-S subbituminous coals from the Teruel Mining district, Northeast Spain, Appl. Geochem. 7 (5) (1992) 547–561.

[7] M.R. Martinez-Tarazona, D.A. Spears, J.M.D. Tascon, Organic affinity of trace elements in Australian bituminous coals, Fuel 71 (9) (1992) 909–917.

[8] M. Pires, E.C. Teixeira, Geochemical distribution of trace elements in lean coal, Brazil, Fuel 71 (10) (1992) 1093–1096.

[9] D.A. Spears, M.R. Martinez-Tarazona, Geochemical and mineralogical characteristics of a power station feed-coal, Eggbrough, England, Int. J. Coal Geol. 22 (1) (1993) 1–20.

[10] G.E. Mercer, S. Fitzgerald, J. Day, R.H. Filby, Determination of organic/inorganic associations of trace elements in kerogen of the New Albany shale, Fuel 72 (11) (1993) 1187–1195.

[11] S.V. Vassilev, Trace elements in solid waste products from coal burning at some Bulgarian thermoelectric power station, Fuel 73 (3) (1994) 367.

[12] X. Querol, T.J.L. Fernandez, S.A. Lopez, Trace elements in coal and their behavior during combustion in a large station, Fuel 74 (3) (1995) 331–343.

[13] X. Lu, H. Zeng, T. Xu, R. Yan, Chemometric studies of distribution of trace elements in seven Chinese coals, Fuel 74 (12) (1995) 1382–1386.

[14] S. Vassilev, K. Kitano, C.G. Vassilev, Some relationships between coal rank and chemical and mineral composition, Fuel 75 (12) (1996) 1537–1542.

[15] F.K. Huggins, F. Goodarzi, C.J. Lafferty, Mode of occurrence of arsenic in subbituminous coals, Energy Fuels 10 (10) (1996) 1001–1004.

[16] I.M. Smith, Trace elements from coal combustion: emissions, Chapter 2, Sources of trace elements, IEACR/01, IEA Coal Research, London, 1987.

[17] F.E. Huggins, N. Shah, G.P. Huffman, A. Kolker, S. Crowley, C.A. Palmer, R.B. Finkelman, Mode of occurrence of chromium in four US coals, Fuel Process. Technol. 63 (2–3) (2000) 79–92.

[18] A. Kolker, F.E. Huggins, C.A. Palmer, N. Shah, S.S. Crowley, G.P. Huffman, R.B. Finkelman, Mode of occurrence of arsenic in four US coals, Fuel Process. Technol. 63 (2–3) (2000) 167–178.

[19] R. Yan, H. Zeng, Z. Ouyang, et al., The mode of occurrence and concentration of trace elements in several typical Chinese coals, Anal. Lab. 14 (4) (1995) 43–47 (In Chinese).

[20] X. Lu, A. Ali, H. Liu, H. Zeng, Multivariable analysis and experimental researches on the distribution of trace elements in coal, Environ. Chem. 14 (6) (1995) 494–499 (In Chinese).

[21] X. Lu, T. Xu, H. Liu, et al., Factor analysis method in study on trace element distribution in coal, J. Fuel Chem. Technol. 22 (4) (1994) 438 (In Chinese).

[22] J.A. Ratafia-Brown, Overview of trace elements partitioning in flames and furnaces of utility coal-fired boilers, Fuel Process. Technol. 39 (2) (1994) 139–157.

[23] W.P. Linak, J.O.L. Wendt, Trace metal transformation mechanisms during coal combustion, Fuel Process. Technol. 39 (2) (1994) 173–198.

[24] J.J. Helble, Trace element behavior during coal combustion: results of a laboratory study, Fuel Process. Technol. 39 (1994) 159–172.

[25] L.B. Clarke, The fate of trace elements during coal combustion and gasification: an overview, Fuel 72 (1993) 731.

[26] L.E. Bool, J.J. Helble, A laboratory study of the partitioning of trace elements during pulverized coal combustion, Energy Fuels 9 (1995) 880–887.

[27] G.A. Norton, A review of trace element emission from the combustion of refuse-derived fuel with coal, Environ. Prog. 11 (2) (1992) 140–144.

[28] B.S. Haynes, M. Neville, R.J. Quann, A.F. Sarofim, Factors governing the surface enrichment of fly ash in volatile trace species, J. Colloid Interface Sci. 87 (1) (1982) 266–278.

[29] R.J. Quann, M. Neville, M. Janghorbani, C.A. Mims, A.F. Sarofim, Mineral matter and trace-element vaporization in a laboratory-pulverized coal combustion system, Environ. Sci. Technol. 16 (7) (1982) 776–781.

[30] E.A. Korzun, H.H. Heck, Sources and fates of lead and cadmium in municipal solid waste, J. Air Waste Manage. Assoc. 40 (9) (1990) 1220–1226.

[31] E.I. Kauppinen, T.A. Pakkanen, Coal combustion aerosols: a field study, Environ. Sci. Technol. 24 (6) (1990) 1811–1818.

[32] P.C. Siebert, D. Alston-Guiden, Air toxics emissions from municipal, hazardous and medical waste incinerators and the effects of control equipment, 84th Annual Meeting of Air and Waste Manage. Assoc., Vancouver, British Columbia, 1991.

[33] E.C. Teixeira, J.C. Samama, A. Brun, Study of the concentration of trace elements in fly-ash resulting from coal combustion, Environ. Technol. 13 (9) (1992) 995–1000.

[34] R.G. Rizeq, W. Clark, W.R. Seeker, Analysis of toxic metals emissions from waste combustion devices, Proc. of 11th Int. Conf. on Therm. Treat. Radioact. Hazard. Chem. Mined Med. Waste, 1992.

[35] W. Maenhaut, O. Royset, M. Vadset, E.I. Kauppinen, T.M. Lind, Analysis of size-fractionated coal combustion aerosols by PIXE and other analytical techniques, Nucl. Instrum. Methods Phys. Res. B75 (1993) 266–272.

[36] T. Lind, E.I. Kauppinen, J.K. Jokiniemi, A field study on the trace metal behavior in atmospheric circulating fluidized-bed coal combustion, 25th Symp. (Int.) on Combust., The Combustion Institute, Pittsburgh, 1994, pp. 201–209.

[37] H. Manninen, A. Perkio, J. Palonen, K. Peltola, J. Ruuskanen, Trace metal emissions from co-combustion of refuse derived and packaging derived fuels in a circulating fluidized bed boiler, Chemosphere 32 (12) (1996) 2457–2469.

[38] C.L. Senior, T. Zeng, et al., Distribution of trace elements in selected pulverized coals as a function of particle size and density, Fuel Process. Technol. 63 (2–3) (2000) 215–241.

[39] J.C. Kramlich, G.H. Newton, Influence of coal rank and pretreatment on residual ash particle size, Fuel Process. Technol. 37 (1) (1994) 143–161.

[40] M.J. Mcnallan, G.J. Yurek, J.F. Elliott, The formation of inorganic particulates by homogeneous nucleation in gases produced by combustion of coal, Combust. Flame 42 (1981) 45–60.

[41] W.P. Linak, T.W. Peterson, Mechanisms gaverning the composition and size distribution of ash aerosol in a laboratory pulverized coal combustor, 2lst Symposium (International) on Combustion Institute, 1986, pp. 399–410.

[42] H.B. Booher, D.V. Martello, J.P. Tamilia, G.A. Irdi, Microscopic study of spheres and microspheres in fly ash, Fuel 73 (2) (1994) 205–213.

[43] K.K. Rink, J.A. Kozinski, J.S. Lighty, Biosludge incineration in FBCs: behavior of ash particles, Combust. Flame 100 (1995) 121–130.

[44] L.J. Wibberley, T.F. Wall, An investigation of factors affecting the physical characteristics of fly ash formed in a Laboratory Scale Combustor, Combust. Sci. Technol. 48 (1986) 177–190.

[45] A.W. Andren, D.H. Klein, Y. Talmi, Selenium in coal-fired steam plant emissions, Environ. Sci. Technol. 9 (9) (1975) 856–858.

[46] J.G.T. Bergstrom, Mercury behavior in flue gases, Waste Manag. Res. 4 (1986) 57–64.

[47] J.M. Pacyna, Atmospheric emissions of arsenic, cadmium, lead and mercury from high temperature processes in power generation and industry, lead, mercury, cadmium and arsenic in the environment, in: T.C. Hutchinson, K.M. Meema (Eds.), Scope, Wiley, New Jersey, 1987.

[48] M.S. Germani, W.H. Zoller, Vapor-phase concentrations of arsenic selenium, bromine, iodine, and mercury in the stack of a coal-fired power plant, Environ. Sci. Technol. 22 (10) (1988) 1079–1085.

[49] B. Hall, P. Schager, O. Lindqvist, Chemical reactions of mercury in combustion flue gases, Waste Air Soil Pollut. 56 (1) (1991) 3–14.

[50] K.C. Galbreath, C.J. Zygarlicke, Mercury speciation in coal combustion and gasification flue gases, Environ. Sci. Technol. 30 (8) (1996) 2421–2426.

[51] D. Laudal, B. Nott, T. Brown, R. Roberson, Mercury speciation methods for utility flue gas, Fresenius' J. Anal. Chem. 358 (3) (1997) 397–400.

[52] B. Wu, T.W. Peterson, F. Shadman, C.L. Senior, J.R. Morency, et al., Interactions between vapor-phase mercury compounds and coal char in synthetic flue gas, Fuel Process. Technol. 63 (2–3) (2000) 93–107.

[53] C.L. Senior, L.E. Bool III, J.R. Morency, Laboratory study of trace element vaporization from combustion of pulverized coal, Fuel Process. Technol. 63 (2–3) (2000) 109–124.

[54] C.L. Senior, L.E. Bool III, et al., Pilot scale study of trace element vaporization and condensation during combustion of a pulverized sub-bituminous coal, Fuel Process. Technol. 63 (2–3) (2000) 149–165.

[55] W.S. Seames, J.O.L. Wendt, Partitioning of arsenic, selenium, and cadmium during the combustion of Pittsburgh and Illinois #6 coals in a self-sustained combustor, Fuel Process. Technol. 63 (2–3) (2000) 179–196.

[56] C.L. Senior, A.F. Sarofim, et al., Gas-phase transformations of mercury in coal-fired power plants, Fuel Process. Technol. 63 (2–3) (2000) 197–213.

[57] R.B. Finkelman, C.A. Palmer, M.R. Krasnow, P.J. Aruscavage, G.A. Sellers, F.T. Dulong, Combustion and leaching behavior of elements in the Argonne Premium coal samples, Energy Fuels 4 (1990) 755–766.

[58] G.P. Huffman, F.E. Huggins, N. Shah, J. Zhao, Speciation of arsenic chromium in coal and combustion ash by XAFS spectroscopy, Fuel Process. Technol. 39 (1994) 47–62.

[59] T.T. Eighmy, J.D. Eusden, K. Marsella, Particle petrogenesis and speciation of elements in MSW incineration bottom ashes, in: J.J.J.M. Goumans, H.A. Van Der Sloot, Th.G. Aalbers (Eds.), Environmental Aspects of Construction with Waste Materials, 1994, pp. 111–136.

[60] P. Quevauviller, G. Raurert, H. Muntau, A.M. Ure, R. Rubio, J.F. Lopez-Sanchez, H.D. Fiedler, B. Grieping, Evaluation of a sequential extraction procedure for the determination of extractable trace metal contents in sediments, Fresenius' J. Anal. Chem. 349 (1994) 808–814.

[61] A.K. Das, R. Chakraborty, M.L. Cervera, M. Guardia, Metal speciation in solid matrices, Talanta 42 (1995) 1007–1030.

[62] X. Querol, R. Juan, A. Lopez-Soler, J.L. Fernandez-Turiel, C.R. Ruiz, Mobility of trace elements from coal and combustion wastes, Fuel 75 (7) (1996) 821–838.

[63] EDF, Physico-Chemical Characterization and Leaching of Desulphurization Coal Fly Ash, Collection de notes internes de la Direction des Etudes et Recherches, EDF (Electricite de France), 96NV00029(HE-35/95.022), ISSN 1161-0573, 1996.

[64] EDF, Circulating Fluidised Bed Combustion Ash Characterization: the Case of the Provence 250 MW Unit, Collection de notes internes de la Direction des Etudes et Recherches, EDF (Electricite de france), 97NB00091 (HE-35/97/10), ISSN 1161-0611, 1997.

[65] P.H. Brunner, H. Monch, The flux of metals through municipal solid waste incinerators, Waste Manag.Res. 4 (1986) 105–119.

[66] T.L. Clapp, J.F. Magee II, R.C. Ahlert, D.S. Kosson, Municipal solid waste composition and the behavior of metals in incineration ashes, Environ. Prog. 7 (1) (1998) 22–30.

[67] E.G. Eddings, J.S. Lighty, Fundamental studies of metal behavior during solid incineration, Combust. Sci. Technol. 85 (1992) 375–390.

[68] S.C. Saxena, C.K. Jotshi, Fluidized-bed incineration of waste materials, Pror. Energy Combust. Sci. 20 (1994) 281–324.

[69] F. Hasselriis, A. Licata, Analysis of heavy metal emission data from municipal waste combustion, J. Hazard. Mater. 47 (1996) 77–102.

[70] R.J. Quann, A.F. Sarofim, Vaporization of refractory oxides during pulverized coal combustion, 19th Symp. (Int.) on Combust., The Combustion Institute, Pittsburgh, 1982, pp. 1429–1440.

[71] L.L. Baxter, R.E. Mitchell, The release of iron during the combustion of Illinois no.6 coal, Combust. Flame 88 (1) (1992) 1–14.

[72] T.C. Ho, H.T. Lee, C.C. Shiao, J.R. Hopper, Metal behavior during fluidized bed thermal treatment of soil, Waste Manage. 15 (3) (1995) 325–334.

[73] T.C. Ho, H.T. Lee, C.C. Shiao, J.R. Hopper, Metal behavior during fluidized bed thermal treatment of soil, Waste Manage. 15 (1995) 325–334.

[74] A. Jakob, S. Stucki, P. Kuhn, Environ. Sci. Technol. 29 (9) (1995) 2429–2436.

[75] C.L. Senior, Development of a mechanistic model for prediction of emission of trace elements from coal-fired power plants, Fuel Process. Technol. 63 (2–3) (2000) 75–77.

[76] J.J. Helble, A model for the air emissions of trace metallic elements from coal combustors equipped with electrostatic precipitators, Fuel Process. Technol. 63 (2–3) (2000) 125–147.

[77] F.M. Gelbrad, J.H. Seinfeld, J. Colloid Interface Sci. 63 (3) (1978) 472–479.

[78] F.M. Gelbrad, J.H. Seinfeld, J. Colloid Interface Sci. 68 (2) (1979) 363–382.

[79] F.M. Gelbrad, J.H. Seinfeld, J. Colloid Interface Sci. 78 (2) (1980) 485–501.

[80] M. Neville, A.F. Sarofim, The stratified composition of inorganic submicron particles produced during coal combustion, 19th Symp. (Int.) on Combust., The Combustion Institute, Pittsburgh, 1982, pp. 1441–1449.

[81] T. Matsoukas, S.K. Friedlander, J. Colloid Interface Sci. 146 (2) (1991) 495–506.

[82] W.Y. Lin, V. Stehi, P. Biswas, Aerosol Sci. Tech. 17 (1992) 119–133.

[83] A.R. Manzoori, P.K. Agarwal, Fuel 72 (7) (1993) 1069–1075.

[84] K.C. Galbreath, C.J. Zygarlicke, Environ. Sci. Technol. 30 (8) (1996) 2421–2426.

[85] B. Hall, P. Schager, J. Weesmaa, Chemosphere 30 (1995) 611–627.

[86] N.C. Widmer, J. West, Thermochemical study of mercury oxidation in utility boiler fuel gases, 93rd Annual Meeting, Air and Waste Management Association, Salt Lake City, Utah, 2000.

[87] C.L. Senior, A.F. Sarofim, T. Zeng, J.J. Helble, R. Mamani-Paco, Fuel Process. Technol. 63 (1999) 197–213.

[88] N.R. Sliger, J.D. Going, J.C. Kramlich, Kinetic investigation of the high-temperature oxidation of mercury by chlorine species, in: J.R. Edwards, R.K. Srivastava, J.D. Kilgroe (Eds.), Western State Section/The Combustion Institute, Fall Meeting, Seattle 1998, J. Air and Waste Manage. Assoc., vol. 51, 2001, pp. 869–877.

[89] J.R. Edwards, R.K. Srivastava, J.D. Kilgroe, J. Air Waste Manage. Assoc. 51 (2001) 869–877.

[90] S. Niksa, J.J. Helble, N. Fujiwara, Kinetic modeling of homogeneous mercury oxidation: the importance of NO and H_2O in predicting oxidation in coal-derived systems, Environ. Sci. Technol. 35 (2001) 3701–3706.

[91] M. Xu, Y. Qiao, C. Zheng, L. Li, J. Liu, Modeling of homogeneous mercury speciation using detailed chemical kinetics, Combust. Flame 132 (2003) 208–218.

[92] R. Feng, M. Xu, Y. Qiao, J. Cheng, C. Yao, J. Zhan, Study on mechanism of mercury oxidation in combustion generated flue gas, J. Eng. Thermophys. 23 (2002) 384–387.

[93] Y. Qiao, M. Xu, J. Cheng, C. Sheng, C. Zheng, The oxidation kinetics of mercury in Hg/O/H/Cl system, Fuel Process. Technol. (submitted for publication).

[94] S. Yu, I.M. Kennedy, A preliminary kinetic model of chromium in a hydrogen/air flame, Combust. Sci. and Tech. 160 (2000) 38.

[95] J. Cheng, M. Xu, H. Zeng, S. Hu, P. Li, Y. Qiao, R. Feng, The oxidation kinetics of chromium at high temperature: the reactions of Cr/O_2, Int. Conf. on Energy Conversion and Application, Wuhan, China, 2001, pp. 748–751.

[96] K. Carlsson, Heavy metals from "Energy from Waste" plants—comparison of gas cleaning system, Waste Manag. Res. 4 (1) (1986) 15–20.

[97] Y. Otani, C. Kanaoka, C. Usui, S. Matsui, H. Emi, Environ. Sci. Technol. 20 (7) (1986) 735–738.

[98] H. Vogg, H. Braun, M. Metzger, J. Schneider, Waste Manag. Res. 4 (1986) 65–74.

[99] Y. Otani, H. Emi, C. Kanaoka, I. Uchijima, H. Nishino, Environ. Sci. Technol. 22 (6) (1988) 708–711.

[100] A. Lancia, D. Musmarra, F. Pepe, G. Volpicelli, Adsorption of mercury chloride vapors from incinerator flue gases on calcium hydroxide particles, Combust. Sci. Technol. 93 (2) (1993) 277–289.

[101] J.R. Donnelly, Metal emissions control technologies for waste incineration, Clean Energy from Waste and Coal, American Chemical Society, 1993, 0097-6156/93/0515.

[102] B.J. Stuart, D.S. Kosson, Combust. Sci. Technol. 101 (1994) 527–548.

[103] W.P. Linak, R.K. Srivastava, J.O.L. Wendt, Sorbent capture of nickel, lead and cadmium in a laboratory swirl flame incinerator, Combust. Flame 100 (1–2) (1995) 241–250.

[104] C.S. Krivanek, Mercury control technologies for MWC's: the unanswered questions, J. Hazard. Mater. 47 (1) (1996) 163–194.

[105] J.D. Kilgroe, J. Hazard. Mater. 47 (1996) 163–194.

[106] S.V. Krishnan, B.K. Gullett, W. Jozewicz, Mercury control in municipal waste combustors and coal-fired utilities, EPA technical report, EPA/600/A-96/118.

[107] A. Ghosh-Dastidar, S. Mahuli, R. Agnihotri, L.S. Fan, Environ. Sci. Technol. 30 (2) (1996) 447–452.

[108] J.C. Chen, M.Y. Wey, M.H. Yan, J. Environ. Eng. 11 (1997) 1100–1106.

[109] T.C. Ho, K.S. Wang, C.C. Shie, J.R. Hopper, Simultaneous sulfur and metal capture by lime during fluidized bed coal combustion, in: L.S. Fan, T.M. Knowlton (Eds.), Proc. of the 9th Eng. Foundation Conf. on Fluidization, 1998, pp. 17–22, Colorado.

[110] J.F. Cheng, H.C. Zeng, M.H. Xu, The effects of solid absorbents on the emission of trace elements, SO_2, and NOx during coal combustion, Int. J. Energy Res. 24 (2001) 1043–1052.

[111] Y. Zhuang, P. Biswas, Submicrometer particle formation during pulverized coal combustion and their control, Proc. 1998 Western States Section Combustion Institute Annual Meeting, Seattle, WA, October 26–28, 1998.

[112] P. Biswas, C.Y. Wu, Control of toxic metal emission from combustors using sorbents: a review, J. Air Waste Manage. Assoc. 48 (1998) 113.

[113] M. Uberoi, F. Shadman, Simultaneous condensation and reaction of metal compound vapors in porous solids, Ind. Eng. Chem. Res. 30 (1991) 624.

[114] B.K. Gullett, K. Raghunathan, Reduction of coal-based metal emissions by furnace sorbent injection, Energy Fuels 8 (1994) 1068–1076.

[115] T.C. Ho, R. Ramanarayan, J.R. Hopper, W.D. Bostick, D.P. Hoffmann, Fluidization VIII, International Symposium of the Engineering Foundation, Tours, France, May 14–19, 1995.

[116] R.M. Martinez-Tarazona, A.D. Spears, Fuel Process. Technol. 47 (1996) 79–92.

[117] H.J. Wouterlood, K.M. Bowling, Environ. Sci. Technol. 13 (1) (1979) 93–97.

[118] S.V. Vassilev, C. Braekman-Danheux, Ph. Laurent, T. Thiemann, A. Fontana, Behaviour, capture and inertization of some trace elements during combustion of refuse-derived char from municipal solid waste, Fuel 78 (1999) 1131–1145.

ELSEVIER Fuel Processing Technology 39 (1994) 173–198

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Trace metal transformation mechanisms during coal combustion

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Abstract

Mechanisms governing the fate of trace metals during coal combustion are reviewed, and new theoretical results interpreting existing data are presented. Emphasis is on predicting the size-segregated speciation of trace metals in pulverized coal-fired power plant effluents. This facet, which determines how trace metals originally in coal impact the environment, is controlled by fuel composition and combustion conditions.

Multicomponent equilibrium calculations are used to predict vaporization/condensation temperatures for antimony, arsenic, beryllium, cadmium, chromium, lead, mercury, nickel, and selenium compounds in coal combustion flue gases, for a representative Illinois No. 6 coal. Experimental data show that equilibrium provides a good guide on the effect of chlorine on the partitioning of pure nickel, cadmium, and lead salts, introduced separately into a gaseous turbulent diffusion flame within an 82 kW combustor. Metal nuclei coagulation mechanisms are examined using existing computer codes, and these predict that coagulation does not allow condensed metal nuclei to be scavenged by existing coal ash particles. Rather, literature data on trace metal enrichment on small particles are consistent with processes of reactive scavenging of metals by larger particles, and it is suggested that these processes might be exploited further to convert these metals into environmentally benign forms.

1. Introduction

This article contains both old and new results, and its purpose is three-fold: first, to elucidate why an understanding of mechanisms governing the fate of trace metals is important; second, to summarize the current understanding of these mechanisms during pulverized coal combustion; and third, to present some new results that help

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Table 1
Metals regulated under RCRA and CAAA

Metal	Symbol	RCRA regulated[a]	CAAA regulated[b]
Antimony	Sb	yes	yes
Arsenic	As	yes	yes
Barium	Ba	yes	no
Beryllium	Be	yes	yes
Cadmium	Cd	yes	yes
Chromium	Cr	yes	yes
Cobalt	Co	no	yes
Lead	Pb	yes	yes
Manganese	Mn	no	yes
Mercury	Hg	yes	yes
Nickel	Ni	yes	yes
Selenium	Se	yes	yes
Silver	Ag	yes	no
Thallium	Tl	yes	no

[a] Appendix VIII regulated as metal and compounds, not otherwise specified. Other specific metal compounds including cyanide compounds of calcium, copper, potassium, sodium, and zinc as well as oxides of vanadium (V) and osmium (VIII) are also regulated [1]. RCRA air emission limits are proposed.

[b] Proposed [2].

quantify the relative importance of some of the various mechanisms considered. This paper's focus is on pulverized coal combustion, and considers mechanistic information on the fate of metals in other systems, only insofar as these shed light onto events pertinent to pulverized coal. The intent is neither to present a copious review of the occurrence of trace metals in coal, nor to review all the trace metal emission data that are available. Rather, the intent is to restrict discussion to mechanisms that can be quantified, and that have the potential to be used to predict the ultimate fate of trace metals in pulverized coal combustion systems.

In the US, two sets of regulations govern air emissions of metals from combustion systems including hazardous waste and municipal waste incinerators. These are the Resource Conservation and Recovery Act (RCRA) [1] and the Clean Air Act Amendments (CAAA) [2] (Table 1). Hazardous waste incinerators (HWIs) and boilers and industrial furnaces (BIFs) which destroy hazardous waste are regulated under RCRA. RCRA regulates metal emissions based on risk assessment arguments which limit the ground level concentrations that may be inhaled by the "most exposed individual". Metals regulated by RCRA include a set of carcinogenic metals (arsenic, beryllium, cadmium, and chromium) and a set of noncarcinogenic metals (antimony, barium, lead, mercury, nickel, selenium, silver, and thallium).

Title III of the CAAA places limits on the emissions of 189 organic and metallic hazardous air pollutants (HAPs) including air emissions from a variety of combustion sources. While at present utility boilers are not included, studies are underway to determine whether these sources should also be regulated. Metals regulated under Title III of the CAAA include antimony, arsenic, beryllium, cadmium, chromium, cobalt, lead, manganese, mercury, nickel, and selenium. While municipal waste incinerators (MWIs) are also regulated under the CAAA, HAP emissions from these sources are specifically exempted. For MWIs, Title III Section 129 requires the Administrator to publish a schedule for the promulgation of emission standards for several substances including numerical emission limits for cadmium, lead, and mercury [2].

There exist copious literature data on the size segregated trace metal content of pulverized coal ash. Table 2 summarizes the results of several authors, and indicates that many of the trace metals of regulatory concern (see Table 1) are concentrated within the submicron particle size fraction. This is important, because these submicron particles are most easily inhaled and deposited in the lungs, and are collected by air pollution control devices with minimum efficiency. The latter point is clearly made in Fig. 1, in which the fly ash particle size distribution before and after an electrostatic precipitator is shown [3]. Note the bimodal distribution. Although the fly ash submicron fraction before particulate control may contain less than 5% of the total mass, it is equal to approximately 50% of the total mass downstream of the electrostatic precipitator. The small particles contain neither the momentum to be removed by impaction nor the high diffusional velocities necessary to migrate to collection surfaces. Improved removal of these small particles, which are often enriched in trace metals, requires advanced high efficiency bag houses or condensing precipitators, and these are uncommon in coal fired utility plants.

Trace metals can be neither created nor destroyed during combustion. However, combustion environments can cause trace metals to be distributed among different particle sizes and species. Of paramount importance, therefore, is not only the size-segregated trace metal concentration, but also the speciation of the trace metal as it enters the environment, either as a solid stream (for landfill or sale) or as an air emission. Although collected power plant ash, whatever its composition and speciation, is currently defined as a "non-hazardous waste" and is exempt from RCRA regulations regarding its disposal, the speciation of trace metals will determine the solubility of any trace metal contained in the ash, and the ease with which it can be isolated from the groundwater and aqueous environments. Combustion may also promote metal reactions with other species, and thus affects metal speciation. For example, glasses containing trace metals and other inorganic species may serve to isolate the trace metals from the environment, and so their formation in the combustion process might be encouraged.

2. Mechanism overview

Fig. 2, adapted from Linak and Wendt [4], shows possible routes along which trace metals are partitioned into vapor, submicron aerosol, and supermicron aerosol. Several paths that pertain specifically to coal are distinguished by thick bold arrows and lines. Trace metals contained in solid or liquid fuels may be chemically bound to

Table 2
Coal combustion investigations describing submicron fly ash elemental enrichment (adapted from Linak and Peterson [35])

Investigation	Submicron enriched	No enrichment trend	Submicron depleted
Biermann and Ondov (1980) [42]	Ba, Se, U, W	Fe, Na	
Coles et al. (1978) [44]	Pb, Ra, Th, U	Ce	
Damle et al. (1982) [45][a]	Sb, As, Cd, Pb, Mo, Se, W, Zn	[b]Ba, Cr, Co, Ni, Mn, Na, Sr, V	[c]Al, Ca, Ce, Hf, Fe, Mg, K, Si, Ti
Davison et al. (1974) [43]	Sb, As, Cd, Cr, Pb, Ni, Se, S, Tl, Zn	Al, Be, C, Fe, Mg, Mn, Si, V	Bi, Ca, Co, Cu, K, Sn, Ti
Desrosiers et al. (1979) [46]	Si, S	Ca, Mg, K, Na	Al, Fe
Flagan and Taylor (1981) [47]	C, Si, Na, S		
Gladney et al. (1976) [48]	Sb, As, Br, I, Pb, Hg, Se	Na	Ce, Fe
Haynes et al. (1982) [38]	Sb, As, Fe, Mn, Hg, K	Mg	Al, Ca, Si
Kaakinen et al. (1975) [49]	Sb, As, Cu, Pb, Mo, Po, Se, Zn	Al, Fe, Nb, Rb, Sr, Y	
Kauppinen and Pakkanen (1990) [50]	Ca, Cd, Cu, Pb, Sr, S, V	Al, Fe, Mg, Mn, Na, Si, Ti, Zn	
Klein et al. (1975) [51][d]	Sb, As, Cd, Cu, Cr, Ga, Pb, Mo, Ni, Se, Na, U, V, Zn	Al, Ba, Ca, Ce, Co, Eu, Hf, Fe, La, Mg, Mn, K, Rb, Sc, Si, Sm, Sr, Ta, Th, Ti	
Linak and Peterson (1986) [35]	As, Pb, K, Na, Zn	Al, Ca, Fe, Mg, Mn, Si, Ti	
Markowski et al. (1980) [3]	Sb, As, Cd, Cr, Ni, Rb, Se, V, Zn	Fe, Ti	Al, Hf, Mg, Mn, Ta
Neville and Sarofim (1982) [37]	Al, Sb, As, Si, Na	Fe, Mg	
Neville et al. (1983) [52]	Al, Sb, As, Cr, Na, Zn	Ca, Fe, Mg	
Ondov et al. (1978) [53]	Sb, As, Ba, Ga, In, Mo, Se, U, V, W, Zn		
Ondov et al. (1979) [54]	Sb, As, Ba, Mo, Se, V, W		
Quann and Sarofim (1982) [55]	Mg, K, Na		
Quann et al. (1982) [56]	Sb, As, Cr, Cl, Co, Mg, P, K, Na, Zn		Al, Sc, Th
Shendrikar et al. (1983) [57]	Sb, As, Cl, Hg, Ni, Se, Zn		Al, Ca, Mg
Smith et al. (1979) [58]	Sb, As, Br, Cu, Cr, Ga, Pb, Hg, Mo, Ni, Se, S, Sn, V, Zn	Fe, Mg	
Smith et al. (1980) [59][e]	As, Cu, Cr, Ga, Ge, Pb, Mo, Ni, Se, Sn, V, Zn	Al, Ba, Ca, Ce, Fe, La, Mn, Nb, K, Rb, Si, Sr, Ti, Y, Zr	

[a] Literature review.
[b] Slight enrichment or no change.
[c] No change or slight depletion.
[d] Species Br, Cl, Hg, Se in vapor phase, high filter penetration.
[e] Species As, Br, Cl, I, Hg, Se in vapor phase, high filter penetration.

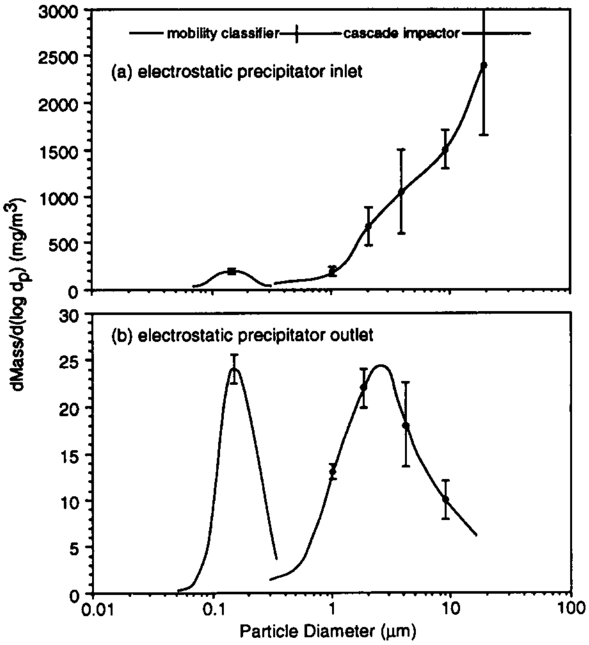

Fig. 1. Comparison of submicron and supermicron particle collection efficiency through a high efficiency electrostatic precipitator (adapted from Markowski et al. [3]).

the organic fuel matrix (inherent inorganic matter), dispersed within the solid fuel particle as minerals (included mineral matter), or as minerals, completely extraneous to the fuel particle (excluded mineral matter). The mode of occurrence of trace metals in coal has a large bearing on which mechanisms are important. Further elaboration on which metals are found in which mode for a variety of coals is outside the scope of this paper, and has been discussed by others [5]. Of interest here is to determine the extent to which variations in the initial form of the trace metal (organic/inherent, included, excluded) affect the subsequent transformation of the metal before it leaves the process. The overriding question is whether the metal will leave the combustor as vapor (as expected for mercury), as submicron particles, which are difficult to collect and isolate from the air environment, or whether it will form or combine with easily collectable large ash particles, which may, either with or without further treatment, be isolated from the aquatic and soil environments.

The behavior of a volatile metal which is initially bound in a char matrix, in close proximity to other inorganic minerals, can be examined indirectly by revisiting the release of another volatile metal, such as sodium initially bound in coal. The release of potassium and sodium during coal combustion has been studied by a number of investigators [6–14] and may shed light on what might be expected for trace metals organically bound in the coal matrix. These studies show (1) sodium bound to carbon in the char is released at temperatures far above the boiling point of a pure sodium

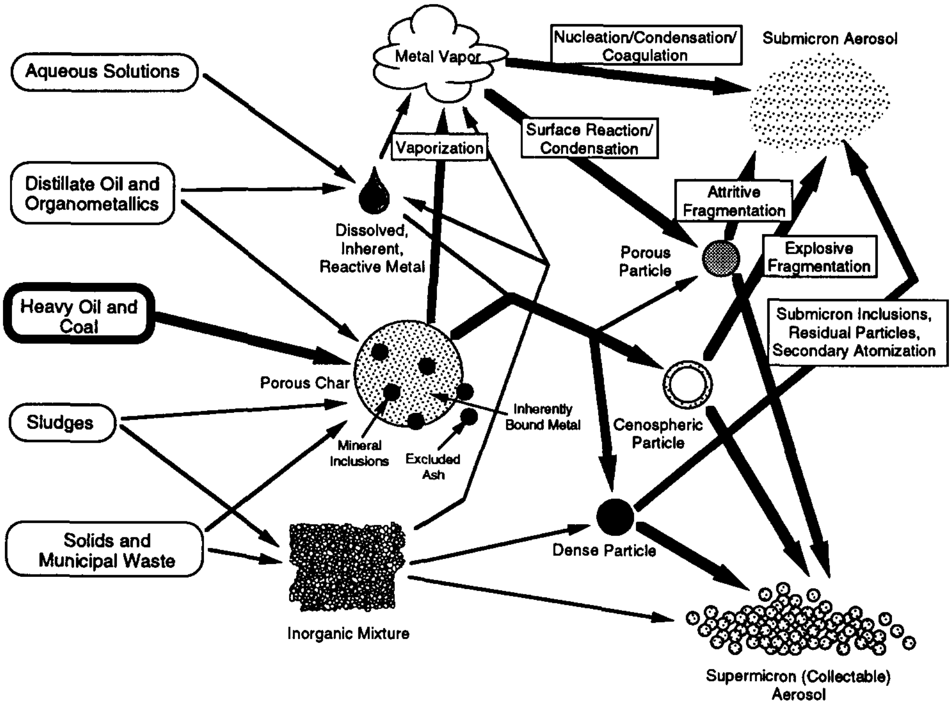
Aqueous Solutions
Distillate Oil and Organometallics
Heavy Oil and Coal
Sludges
Solids and Municipal Waste
Metal Vapor
Vaporization
Nucleation/Condensation/ Coagulation
Submicron Aerosol
Surface Reaction/ Condensation
Attritive Fragmentation
Explosive Fragmentation
Porous Particle
Dissolved, Inherent, Reactive Metal
Submicron Inclusions, Residual Particles, Secondary Atomization
Porous Char
Inherently Bound Metal
Mineral Inclusions
Excluded Ash
Cenospheric Particle
Dense Particle
Inorganic Mixture
Supermicron (Collectable) Aerosol

Fig. 2. Possible controlling mechanisms for particle formation in combustion systems (adapted from Linak and Wendt [4]).

compound; (2) much of the sodium is captured by aluminosilicates and the amount captured increases with increasing temperature, thus causing the amount released as vapor to decrease with increasing temperature; (3) one volatile species, originally bound within a mineral (such as potassium within illite) where it is non-volatile, can be displaced and released by another volatile metal (such as sodium); and (4) the size of the silicate inclusions is also a factor in capturing the volatile metal. Whether some or all of these phenomena occur for trace metals is highly questionable, but they should not be excluded a priori.

3. Equilibrium predictions

As suggested in Fig. 2, a likely, but not the only, mechanism for the formation of small particles enriched in trace metals, is through high-temperature vaporization. Metal constituents may be vaporized as introduced or after transformation within the combustor. Supersaturated vapors may then condense heterogeneously on the surfaces of existing particles or nucleate homogeneously to form new particles. To address this mechanistic route, one might consider the vapor pressures

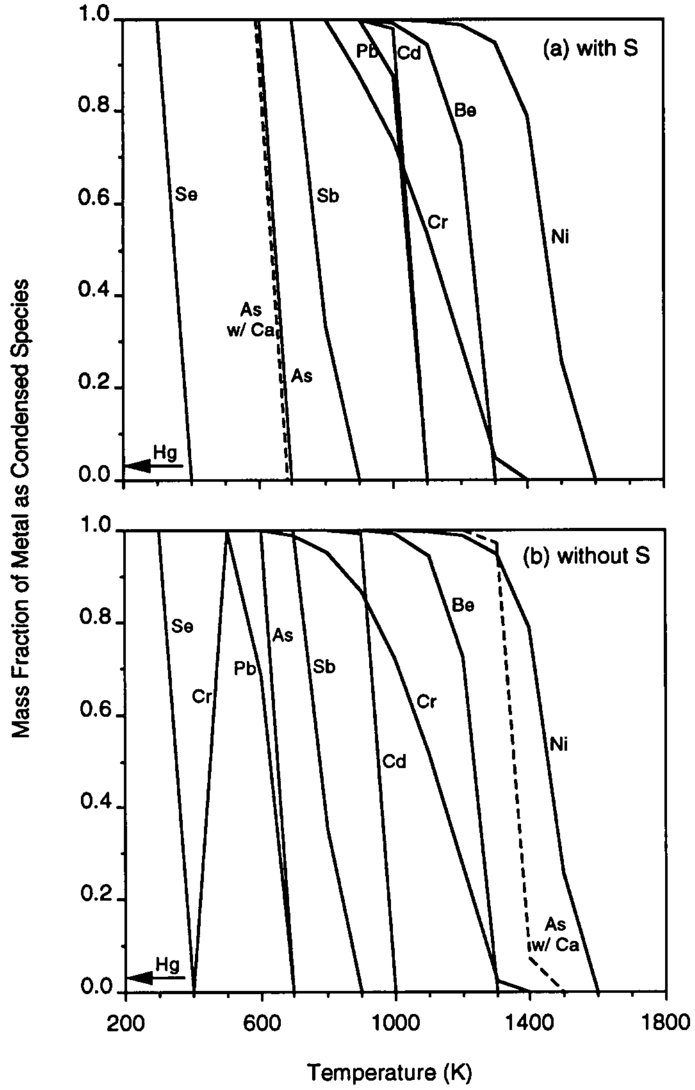

Fig. 3. Equilibrium predictions of condensed trace metal species as a function of temperature in a simulated coal fired utility boiler flue gas environment. Flue gas elemental concentrations calculated for an Illinois No. 6 coal and 20% excess air (Table 3) were used. Trace metal products considered are presented in Table 4. No metal/(metal or silicon) interactions were considered except as noted. Equilibrium predictions (a) with sulfur, and (b) without sulfur are included. Note that no condensed mercury species are predicted above 200 K.

of selected trace metal compounds, since this provides a guide to their potential volatility. Vapor pressures of pure compounds, however, do not show which species are favored according to equilibrium considerations, and do not, by themselves, predict when and under what conditions condensation will occur. Figs. 3(a) and (b) present results from multicomponent equilibria predictions made by the NASA CET89 computer code [15]. This code calculates equilibria among a given list of species, but allows only ideal gas mixtures and pure condensed species, neglecting the possible formation of complex slags and glasses, which are known to be formed [16].

Solutions obtained depend on the species for which thermodynamic data are included, and if an important species containing the element in question is omitted, the prediction will be quite incorrect. Since metal–metal interactions may be important, the calculated solutions are also likely to depend on the mix of metal elements which are specified in the initial mixture. In addition, equilibrium predictions do not account for any kinetic or mixing limitations which may control species formation in practice. However, even with these limitations, equilibrium predictions provide a reasonable starting point to describe the behavior of metals. For the results presented here, the calculations have included antimony, arsenic, beryllium, cadmium, chromium, lead, mercury, nickel, and selenium, however, the equilibrium data set available did not include any compounds of cobalt or manganese, which are, therefore, excluded. Table 3 presents the elemental concentrations used for the equilibrium analyses which were calculated based on the flue gas composition of an Illinois No. 6 bituminous coal and 20% excess air. Trace metal products considered during the equilibrium analyses are presented in Table 4. The trace metals were each examined separately and, unless specifically noted, the equilibrium results presented are in the absence of major metal or silicon species (see Table 3).

Figs. 3(a) and (b) present the mass fraction of predicted condensed species versus temperature for nine trace elements at concentrations found in Illinois No. 6 bituminous coal [17, 18]. In the presence of sulfur (Fig. 3(a)) equilibrium predicts that nickel, beryllium, and chromium are the most refractory, forming condensed species at the highest temperatures. Conversely, mercury, selenium, and arsenic are the most volatile. In fact, these predictions indicate that mercury is unlikely to form any condensed species even at temperatures as low as 200 K. If sulfur is removed from the calculations (Fig. 3(b)) the results are somewhat different. The trace metals are no longer able to form sulfates or sulfides, and are more likely to form chlorides (even from the small amounts of chlorine present) which tend to be more volatile. Fig. 3(b) indicates that several of the curves have shifted to the left (chromium, cadmium, and lead). Chromium is even predicted to form condensed species and then revaporize at lower temperatures. In the absence of sulfur, Fig. 3(b) shows that even relatively small amounts of chlorine keep lead in the vapor form (as $PbCl_2$) until much cooler regions of the combustor are reached. In fact, if the species $PbCl_4$ were also considered as a possible species in the equilibrium calculation, then predictions would allow all of the lead to remain as a vapor at temperatures as low as 200 K. However, Eddings and Lighty [19] noted the absence of $PbCl_4$ in their experimental samples examining incineration of contaminated soils. Nickel condensation is also affected by the presence of chlorine, but compared to lead, the effect is less notable until much higher (percent) chlorine levels are available [4]. In general, the effect of chlorine is to lower the temperature at which there is a transition between vapor and condensed trace metal species. For coal combustion systems, this implies that even a small amount of

Table 3
Elemental concentrations of an Illinois No. 6 bituminous coal used in equilibrium analysis

Ultimate analysis	Wt% in coal[a]
Carbon (C)	59.87
Hydrogen (H)	4.55
Oxygen (O)	8.52
Nitrogen (N)	1.37
Sulfur (S)	3.76
Moisture (H_2O)	13.31
Ash	8.62
Total	100.00

[a] Taken from Helble et al. [17].

Fuel/oxidant species	lb mol[b]
C	4.989
H	4.55
O_2	7.9175
N_2	26.928
S	0.118
H_2O	0.739

[b] Basis of 45.36 kg (100 lb) of coal and 20% excess air.

Major metal and silicon species	Wt% in ash[c]
SiO_2	46.1
Al_2O_3	18.0
Fe_2O_3	20.5
CaO	5.3
MgO	0.6
Na_2O	1.3
K_2O	2.1

[c] Taken from Helble et al. [17].

Major metal and silicon elements	lb mol[d]
Si	0.0662
Al	0.0293
Fe	0.0221
Ca	0.00816
Mg	0.00130
Na	0.00361
K	0.00385

[d] Basis of 45.36 kg (100 lb) of coal and 8.62 wt% ash.

Trace elements	ppm in coal[e]	lb mol[f]
Sb	1.04	0.000000852
As	18.3	0.0000244
Be	1.63	0.0000181
Cd	0.66	0.000000589
Cr	32.8	0.0000631
Co	8.76	0.0000148
Pb	28.4	0.0000137
Mn	124	0.000225
Hg	0.14	0.0000000700
Ni	25.7	0.0000436
Se	1.66	0.00000210
Cl	1200[g]	0.00343

[e] Parts per million by weight. Taken from DeVito et al. [18].
[f] Basis of 45.36 kg (100 lb) of coal.
[g] Taken from Helble et al. [17].

Table 4
Trace metal products considered during equilibrium analysis[a]

Metal	Products without sulfur	Additional sulfur products
Antimony	Sb, Sb_2, Sb_4, SbCl, $SbCl_3$, $SbCl_5$, SbH_3, SbO, Sb_4O_6, Sb(s), Sb(l), $SbCl_3$(s), $SbCl_3$(l), Sb_2O_3(s − a), Sb_2O_3(s − b), Sb_2O_3(l), Sb_2O_3[o](s), Sb_2O_4(s), Sb_2O_5(s), SbOCl(s)	SbS, Sb_2S_3, Sb_2S_4, Sb_3S_2, Sb_4S_3, Sb_2S_3(s), Sb_2S_3(l), $Sb_2(SO_4)_3$(s)
Arsenic[b]	As, As_2, As_3, As_4, $AsCl_3$, AsH_3, AsO, As_4O_6, As(s), $AsCl_3$(l), As_2O_3(s), As_2O_3(l), As_2O_3[a](s), As_2O_5(s)	AsS, As_4S_4, As_2S_2(s), As_2S_2(l), As_2S_3(s1), As_2S_3(s2), As_2S_3(l), As_4S_4(s), As_4S_4(l)
Beryllium	Be, BeCl, $BeCl_2$, BeH, BeN, BeO, BeOH, BeO_2H_2, Be_2Cl_4, Be_2O, Be_2O_2, Be_3O_3, Be_4O_4, Be(s), Be(l), $BeCl_2$(s), $BeCl_2$(l), BeO(a), BeO(l), BeO_2H_2(b), Be_2C(s), Be_2C(l)	BeS, BeS(s), $BeSO_4$(s − a), $BeSO_4$(s − b), $BeSO_4$(s − c)
Cadmium	Cd, CdO, Cd(s), Cd(l), $CdCO_3$(s), $CdCl_2$(s), $CdCl_2$(l), CdO(s), $Cd(OH)_2$(s)	CdS, CdS(s), $CdSO_4$(s − a), $CdSO_4$(s − b), $CdSO_4$(s − 1)
Chromium	Cr, CrCl, $CrCl_2$, CrOCl, $CrCl_3$, $CrOCl_2$, $CrCl_4$, CrO_2Cl, $CrOCl_3$, $CrCl_5$, CrO_2Cl_2, $CrOCl_4$, $CrCl_6$, CrN, CrO, CrOH, CrO_2, CrOOH, $Cr(OH)_2$, CrO_3, CrO_2OH, $Cr(OH)_3$, $CrO(OH)_2$, $CrO_2(OH)_2$, $Cr(OH)_4$, $CrO(OH)_4$, $Cr(OH)_5$, $Cr(OH)_6$, Cr(s), Cr(l), Cr_7C_3(s), $Cr_{23}C_6$(s), $Cr(CO)_6$(s), $CrCl_2$(s), $CrCl_2$(l), $CrCl_3$(s), CrN(s), Cr_2N(s), CrO_2(s), CrO_3(s), CrO_3(l), Cr_2O_3(s), Cr_2O_3(l)	CrS(1), CrS(2), $Cr_2(SO_4)_3$(s)
Cobalt	Co compounds were not included in the available data set.	
Lead[c]	Pb, PbCl, $PbCl_2$, PbO, Pb_2, Pb(s), Pb(l), $PbCl_2$(s), $PbCl_2$(l), PbO(rd), PbO(yw), PbO(l), PbO_2(s), Pb_3O_4(s)	PbS, PbS(s), PbS(l), $PbSO_4$(1), $PbSO_4$(2), $PbSO_4$(l)
Manganese	Mn compounds were not included in the available data set.	
Mercury	Hg, HgCl, $HgCl_2$, HgO, Hg(l), HgO(s)	HgS
Nickel	Ni, NiCl, $NiCl_2$, NiO, NiO_2H_2, Ni(a), Ni(b), Ni(l), $NiCl_2$(s), NiO(1), NiO(2), NiO(3)	NiS, NiS(a), NiS(b), NiS(l), $NiSO_4$(s), NiS_2(s), NiS_2(l), Ni_3S_2(1), Ni_3S_2(2), Ni_3S_2(l), Ni_3S_4(s)
Selenium	Se, $SeCl_2$, SeO, SeO_2, Se_2, Se_2Cl_2, Se(s), Se(l), $SeCl_4$(s), SeO_2(s), Se_2Cl_2(l)	None included in the available data set.

[a] Unless otherwise noted, major metal and silicon compounds were not included, and therefore, formation of silicates, aluminosilicates, or similar species which are known to occur were not predicted.

[b] Separate equilibrium calculations were performed with As in the presence of Ca to investigate the possible formation of calcium arsenate [$Ca_3(AsO_4)_2$(s)].

[c] $PbCl_4$ omitted from data set.

chlorine will enhance the vaporization of metals at low temperatures, and subsequently delay their nucleation and condensation.

To illustrate the potential importance of metal–metal interactions, a set of equilibrium calculations were performed with arsenic and calcium together (with and without sulfur) in order to examine the possible formation of calcium arsenate [$Ca_3(AsO_4)_2(s)$]. In the presence of sulfur (Fig. 3(a)), this compound is not predicted to be formed. However, in the absence of sulfur (Fig. 3(b)) calcium arsenate is predicted to be a preferred product. As a result of the refractory nature of calcium arsenate, this scenario predicts that arsenic will behave similarly to nickel with respect to volatility, and is less likely to be vaporized to form a submicron fume. Consequently, arsenic in the presence of calcium (without sulfur) can be precipitated out as a solid at high temperatures (1400 K compared to 700 K).

The partitioning of chromium is important, since hexavalent species, denoted by dashed lines in Figs. 4(a) and (b), have been shown to be potent carcinogens, while trivalent forms produce other toxic qualities. To illustrate the behavior of chromium in more detail, Figs. 4(a) and (b) present the mass fractions of individual species predicted to be stable as a function of temperature. In the presence of sulfur, chromium forms a variety of oxides, oxyhydroxides, oxychlorides, and sulfates. Note that chromium sulfate [$Cr_2(SO_4)_3(s)$] is the predominant species at low temperatures. In the presence of sulfur, only two hexavalent species [$CrO_2(OH)_2$, CrO_3] are predicted to be stable in notable quantities, and these species are not predicted to be stable at stack temperatures. In the absence of sulfur (Fig. 4(b)), however, vapor phase chloride and oxychloride species are predicted to be stable at low (stack) temperature. Note that both of these species ($CrCl_6$, $CrOCl_4$) are hexavalent forms. While an equilibrium analysis such as this has severe limitations, it does illustrate the importance of considering multiple effects and interaction between trace metals and other species present in coal. Sulfur removal from coal may promote undesirable effects elsewhere.

4. Experimental data on metal aerosol emissions from a swirl flame combustor

Linak et al. [20] have conducted experiments designed to shed insight into mechanisms governing the fate of nickel, cadmium, and lead during combustion. The metals were contained in aqueous salt (nitrate) solutions, which were atomized and injected into a natural gas turbulent diffusion flame. Clearly, this situation is far removed from how these metals might behave during pulverized coal combustion. However, these relatively simple experiments allow specific mechanisms and effects to be isolated (and compared to theory) without the added complications of (unknown or difficult to quantify) reactions with aluminosilicates and/or calcium compounds, for example.

The 82 kW (280,000 Btu/h) combustor, stabilized gaseous turbulent diffusion flames on an International Flame Research Foundation (IFRF) movable block burner [21]. Two different particle sizing instruments were used, namely, a differential mobility particle sizer (DMPS) for the submicron particle size distributions, and a 30 lpm Andersen cascade impactor for the larger particle size distributions. Care

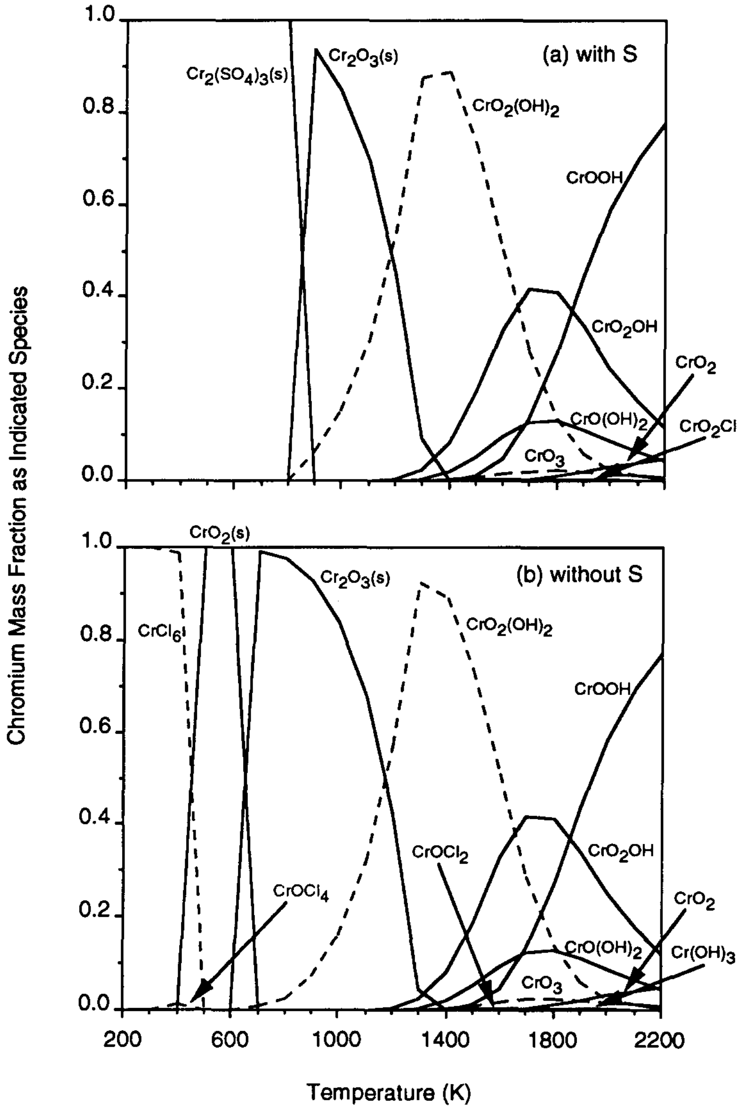

Fig. 4. Equilibrium predictions of chromium species as a function of temperature in a simulated coal fired utility boiler flue gas environment. Flue gas elemental concentrations calculated for an Illinois No. 6 coal and 20% excess air (Table 3) were used. Chromium products considered are presented in Table 4. No metal/(metal or silicon) interactions were considered. Equilibrium predictions (a) with sulfur, and (b) without sulfur are included.

was taken in designing the particle sampling probes, and the subsequent dilution systems that were necessary to be compatible both with the appropriate instrument, and the need to extract a representative sample. Details of the experimental equipment and sampling and analysis system can be found elsewhere [20, 22].

Results, shown in Fig. 5, show some interesting mechanistic phenomena. Data is presented showing both the submicron and the supermicron particle size distributions (PSDs), with and without chlorine present. Without chlorine, and in the absence of other ash particles, volatile metals such as cadmium and lead form a submicron fume with a mass mean diameter of approximately 0.1 μm. This small particle diameter suggests that, even in turbulent diffusion flames, it is difficult to coagulate nuclei to form large collectable particles by themselves. Non-volatile metals such as nickel form much larger particles, and the PSD is consistent with residual metal particles formed from one particle per droplet. The effect of chlorine on nickel is profound; the nickel aerosol behaves in an essentially similar manner as the volatile cadmium and lead metals. The conclusions to be drawn from these data is that for simple systems, where scavenging agents containing calcium, silicon, or aluminum are absent, results predicted from equilibrium considerations appear to be valid, and the influence of chlorine is significant. Therefore, the equilibrium predictions presented above appear to have merit, provided that Table 4 includes all important trace metal compounds.

5. Aerosol dynamics

Depending on the time/temperature history, combustion environment, and the presence of other constituents, a portion of the metals present will likely vaporize at high temperatures near the flame, and subsequently nucleate or condense at lower temperatures downstream. These metals will form a suspended aerosol along with particles which are generated by other mechanisms. These are convected along with the exhaust gases and can undergo various physical transformations which further influence the PSD. The following equation of convective diffusion can be derived to represent a particle material balance over a volume fixed in space:

$$\frac{\partial n}{\partial t} + \nabla \cdot n\boldsymbol{v} = \nabla \cdot D \nabla n - \nabla \cdot n\boldsymbol{c} + R_v \quad (1/\mathrm{m}^3\,\mathrm{s}), \tag{1}$$

where $n(v, x, t)$ $(1/\mathrm{m}^3)$ is the number size distribution, and $n(v, x, t)\,\mathrm{d}v$ is the number of particles per unit volume $(1/\mathrm{m}^3)$ in the particle volume range v to $v + \mathrm{d}v$, at position x and time t. Particle volume, v, is used, rather than particle diameter d_p, since for many simple theories employed here, total particle volume is a conserved quantity. The gas velocity is given by $\boldsymbol{v}$ (m/s), D is the Fickian particle diffusion coefficient $(\mathrm{m}^2/\mathrm{s})$, and $\boldsymbol{c}$ is the particle migration velocity resulting from external forces including gravity (m/s). $R_v(n, x, t)$ is an important term, and represents the net source of particles of size v, at position x, and time t, and includes several other internal physical processes which generate those particles. These internal processes include: nucleation, which allows the formation of new particles directly from the gas phase; coagulation, which leads to particle growth due to particle adhesion or agglomeration, thus changing the PSD, while conserving the total volume (or mass) of particles; and

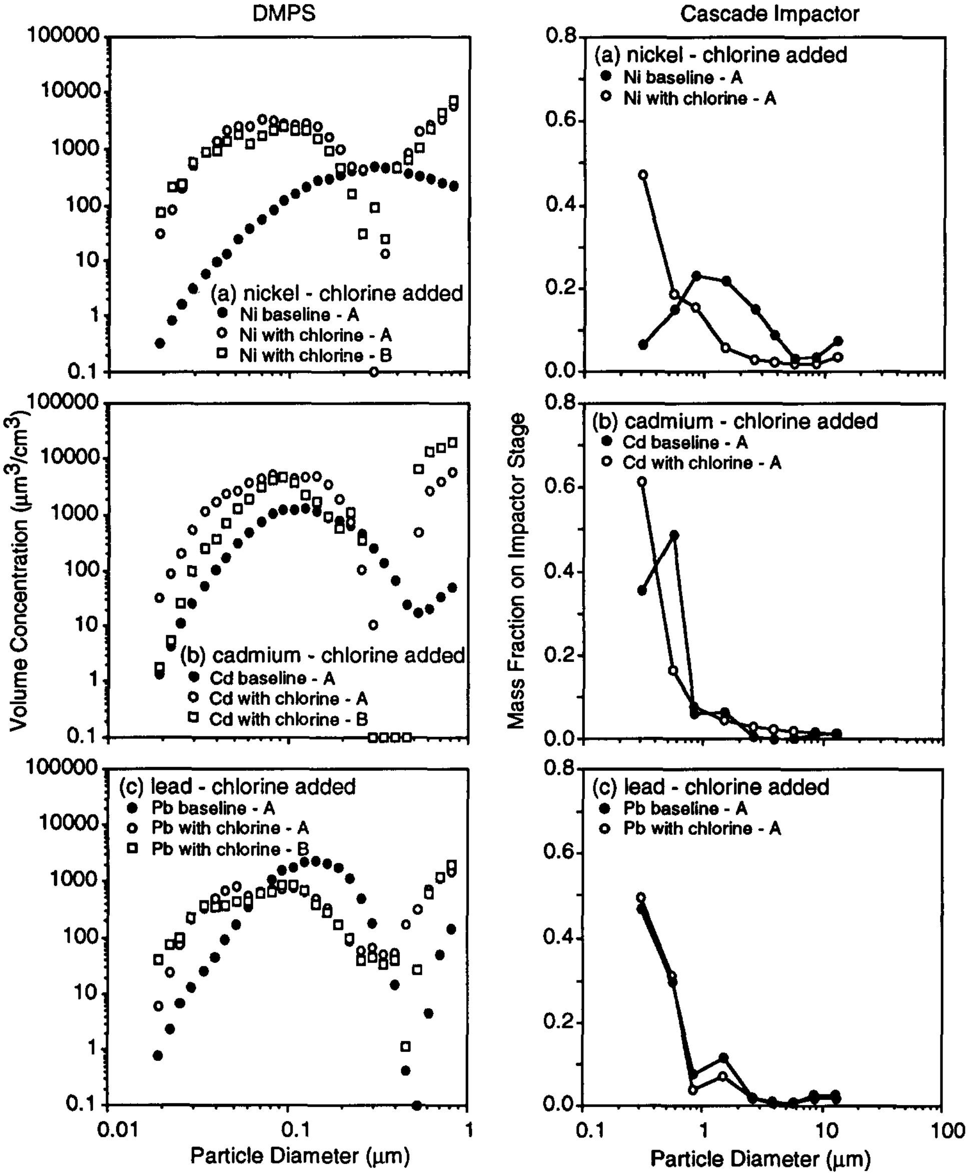

Fig. 5. Baseline and chlorine addition DMPS particle volume distributions and cascade impactor particle mass distributions for (a) nickel, (b) cadmium, and (c) lead. Replicate DMPS distributions are denoted A and B (open symbols). Baseline (without chlorine addition) DMPS and cascade impactor distribution (solid symbols) are included for comparison.

condensation, which changes the PSD because of particle growth caused by mass transfer from the gas phase to an existing condensed phase. Thus

$$R_v = R_{\mathrm{nucl}} + R_{\mathrm{coag}} + R_{\mathrm{cond}} \quad (1/\mathrm{m}^3\mathrm{s}). \tag{2}$$

Before Eq. (1) (to yield the PSD as a function of time and position) can be solved, appropriate descriptions of each of the three terms on the right side of Eq. (2) are required.

5.1. Nucleation

Theoretical expressions for the rate of nucleation have been derived from first principles [23] and depend on S_i, the supersaturation ratio (P_i/P_i^{sat}), as follows:

$$R_{\mathrm{nucl}} = A\exp\left(\frac{-\mathrm{B}}{(\ln S_i)^2}\right) \quad \text{when } d_\mathrm{p} = d_\mathrm{p}^* \quad (1/\mathrm{m}^3\,\mathrm{s}) \tag{3}$$

and

$$R_{\mathrm{nucl}} = 0 \quad \text{when } d_\mathrm{p} \neq d_\mathrm{p}^* \quad (1/\mathrm{m}^3\mathrm{s}). \tag{4}$$

A and B depend on temperature, surface tension, droplet mass, monomer partial pressure, and liquid density. d_p^* is the critical nucleus size, given by

$$d_\mathrm{p}^* = \frac{4\sigma M_{wi}}{\rho_i RT \ln S_i} \quad (\mathrm{m}), \tag{5}$$

where $S_i = P_i/P_i^{\mathrm{sat}}$ is again the supersaturation ratio, σ the surface tension, ρ_i the density of the liquid, M_{wi} the molecular weight of the metal, T the absolute temperature and R the gas constant. Clusters smaller than d_p^* tend to evaporate, while clusters larger than d_p^* tend to grow.

From a practical point of view one should note that the rate at which nuclei are produced is extremely sensitive to the supersaturation ratio, S_i, and to the actual speciation of the metal compound in the gas phase, since this affects not only S_i, but also d_p^*, A, and B in Eq. (3). Scotto [22] has shown that the aerosol size evolution arising from lead vapor nuclei depends strongly on the Pb/PbO ratio in the gas phase, because the nucleation rate is sensitive to speciation.

Eqs. (3) and (4) suggest that the competition between homogeneous nucleation, with a very non-linear dependence on P_i^{sat}, and heterogeneous condensation, which can be shown to have a linear dependence on P_i^{sat}, can be adjusted by varying the temperature quench rates ($\mathrm{d}T/\mathrm{d}t$) in a combustor. Nucleation and condensation of metal vapors in the neighborhood of burning coal particles has been investigated theoretically by Senior and Flagan [24] and Helble et al. [25]. The effect of $\mathrm{d}T/\mathrm{d}t$ has been theoretically investigated by McNallan et al. [26], who suggested that homogeneous nucleation of fine silica may occur at temperatures above 1700 K in spite of the presence, in the gases, of pre-existing particles, when the gases are cooled at a rate in excess of 600 K/s. The experimental data [27] shown in Fig. 6 further support the hypothesis that increased temperature quench rate increases the emission of small nuclei, although these data suggest that the increase was limited to that of sodium fume. This result is in agreement with the results of Taylor and Flagan [28] and Lin et al. [29],

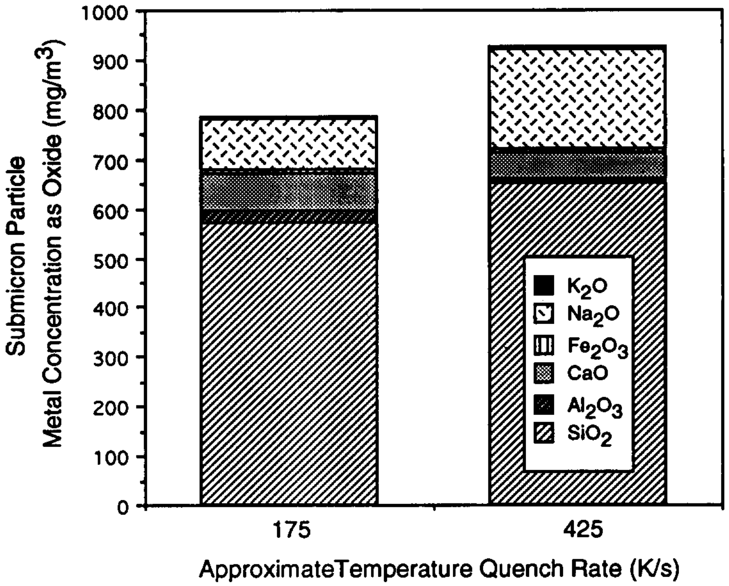

Fig. 6. Effect of temperature quench rate on submicron fly ash particle composition from coal combustion (adapted from Scotto et al. [27]).

in that it suggests that combustion conditions, including temperature quench rate, can have a large influence on the nature of the size-segregated metal aerosol produced.

5.2. Coagulation

Coagulation is a second-order kinetic process where $N_{i,j}$, the number (frequency) of collisions per unit volume and time between particles of sizes i and j, is given by

$$N_{i,j} = \beta_{i,j} n_i n_j \quad (1/\mathrm{m}^3\mathrm{s}) \tag{6}$$

where n_i and n_j are the number concentrations of particles of sizes i and j, respectively ($1/\mathrm{m}^3$) and $\beta_{i,j}$ is the collision frequency (m^3/s), expressions for which are given below (Eqs. (8) and (9)). Using a continuous distribution function, $n(v, x, t)$, defining $\beta(v, v')$ as the collision frequency between particles of sizes v and v', and keeping track of the number of particles of volume v, the rate of formation per unit volume of particles of size v by coagulation can be shown to be [30]

$$R_{\mathrm{coag}} = \frac{1}{2}\int_0^v \beta(v', v - v')n(v', x, t)n(v - v', x, t)\,\mathrm{d}v' - \int_0^\infty \beta(v', v)n(v, x, t)n(v', x, t)\,\mathrm{d}v' \quad (1/\mathrm{m}^3\,\mathrm{s}) \tag{7}$$

Eq. 7 represents the source term describing coagulation for the continuous distribution function in the general dynamic equation (GDE) (Eq. 1). Development of different forms of the collision frequency function, $\beta(v,v')$, is given by Friedlander [30] and depends on the Knudsen number, $Kn = 2l_g/d_p$, where l_g is the gas mean free path, and d_p is the particle diameter. For spherical particles much larger than the gas mean free path ($Kn \ll 1$), particle collision is Brownian diffusion limited, and $\beta(v,v')$ takes the form [31]:

$$\beta(v,v') = 4\pi(D + D')\left(\frac{d_p + d_p'}{2}\right) \quad \text{when } Kn \ll 1 \quad (\mathrm{m^3/s}), \tag{8}$$

where D and D', and d_p and d_p', are the diffusion coefficients (which are low) and diameters, respectively, of the two particles of interest. For particles much smaller than the gas mean free path ($Kn \gg 1$), particle collision is described by the kinetic theory of gases and molecular collision, and yields different coagulation rate coefficients, $\beta(v,v')$, as explained by Fuchs [32]:

$$\beta(v,v') = \left(\frac{3}{4\pi}\right)^{1/6}\left(\frac{6kT}{\rho_p}\right)^{1/2}\left(\frac{1}{v}+\frac{1}{v'}\right)^{1/2}(v^{1/3}+v'^{1/3})^2$$
$$\text{when } Kn \gg 1 \quad (\mathrm{m^3/s}), \tag{9}$$

where ρ_p is the particle density (kg/m^3), and k is the Boltzmann constant. Fuchs [32] also presents expressions for the intermediate regime ($Kn \approx 1$).

Coagulation predictions (coal fly ash)

To predict the PSD evolution due to coagulation, a multicomponent aerosol simulation code (MAEROS) developed by Gelbard and Seinfeld [33] was used. This model solves the GDE (Eq. 1) and can be applied to various environments including an aerosol evolving within a combustion system. Fig. 7 illustrates the predicted evolution of a coal fly ash aerosol due to coagulation only. The MAEROS code was used for a particle size domain (d_p = 0.001–100.0 μm) divided into 15 geometrically equal sections or bins. Coagulation was the only mechanism considered. At time zero, an initial mass of 25 mg/m^3 was assigned to section 2 (d_p = 0.0022–0.0046 μm) to simulate the nucleation of a vaporized fume. Another 475 mg/m^3 was distributed in sections 10–14 (d_p = 1.0–46.4 μm) to simulate the coarse mode fly ash. The composite aerosol was assumed to have the properties of fly ash (ρ = 2.5 g/cm^3), producing a number concentration of 7.5×10^{17} m^{-3}. This initial distribution (see Fig. 7) is based on a fly ash mass concentration of 500 mg/m^3 (before particulate control) allowing 5 percent of the mass to be vaporized to form a submicron fume. The remaining mass (95%) has a mean particle diameter of between 10 and 20 μm. These conditions are consistent with Fig. 1 and literature data [34,35]. System pressure and temperature were maintained at 1.01×10^5 Pa (1 atm) and 810 K (1000°F) to simulate post-flame conditions. Although the code does allow for changes in both pressure and temperature with time, this added complication was not deemed important because of the weak temperature dependence of $\beta(T^{1/2})$. Following the initial distribution, Fig. 7

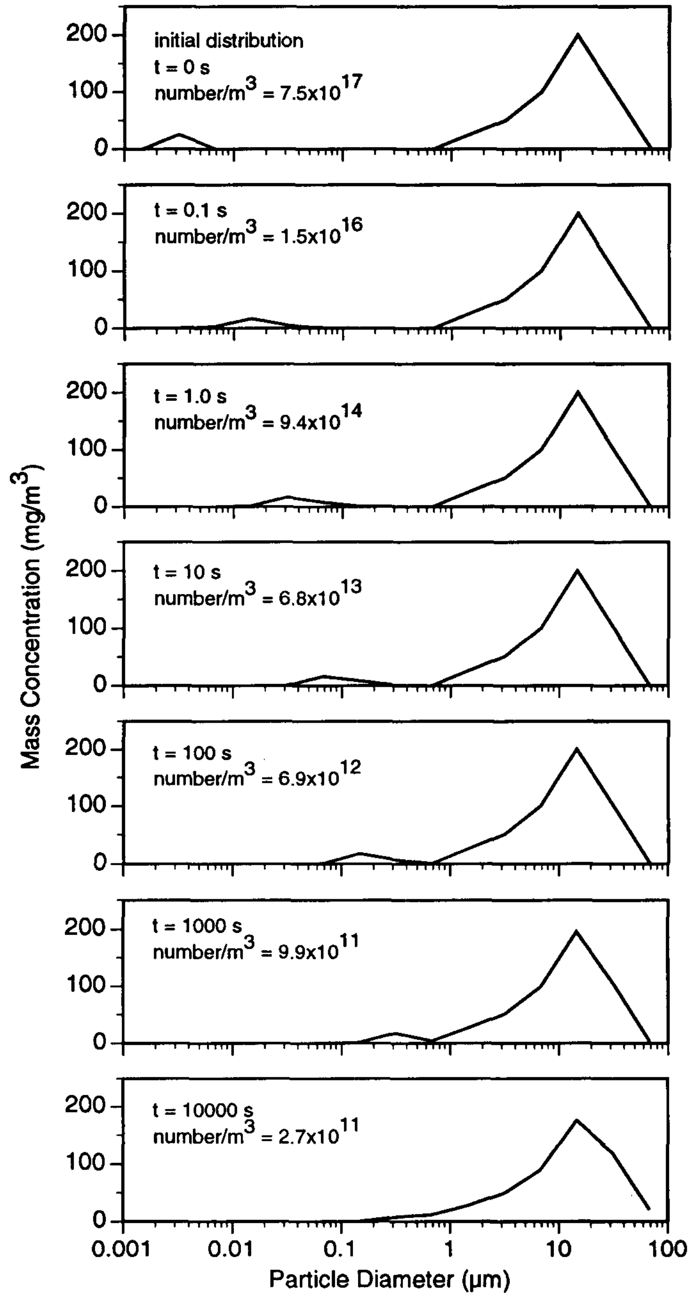

Fig. 7. Predicted evolution of a coal fly ash aerosol via coagulation in a post-flame combustion environment. Initial fly ash concentration of 500 mg/m^3 of which 5% (25 mg/m^3) was assumed to vaporize to form submicron nuclei.

presents six mass distributions which follow the evolving aerosol through six orders in time ($t = 0.1$, 1.0, 10, 100, 1000, 10,000 s). Note that coagulation does not change the total aerosol mass and that the areas under all seven curves represent 500 mg/m^3. Number concentrations, however, are affected and Fig. 7 shows that at 0.1 s the number concentration has fallen almost 2 orders of magnitude (1.5×10^{16} m^{-3}), and the average nuclei particle size has grown (through coagulation) to approximately 0.02 μm. At 1.0 and 10.0 s the nuclei mode distributions have grown slightly further, so that at 10.0 s the nuclei mode produces a mean diameter of between 0.07 and 0.1 μm. This is important, as these times represent a range of typical residence times within coal combustion systems. In fact, even after 10,000 s (2.8 h) the average particle diameter is only approximately 1.0 μm with a number concentration of 2.7×10^{11} m^{-3}.

In summary, aerosol nuclei tend to coagulate very quickly at small times, due to the dependence on two rather large number concentrations (Eq. 7), and then, at larger times, as number concentrations fall, coagulation slows considerably causing the aerosol to accumulate into a mode approximately between $d_p = 0.1$ and 1.0 μm. This conclusion is supported by the experimental data presented in Fig. 5. As discussed previously, particles in this size range exhibit minimum collection efficiencies in most air pollution control devices. This characteristic distribution of a coagulating aerosol has been termed the accumulation mode. Note that the coagulation mechanism does not include the effect of differing fractal properties of the agglomerate formed, as developed by Matsoukas and Friedlander [36] and for this illustration, a fractal dimension of 3 (spheres) was assumed.

Also evident from Fig. 7 is that coagulation between the evolving nuclei mode and the coarse mode is insignificant. Again, this is due in part to the large differences in number concentrations. At time zero, nuclei are present in concentrations of approximately 7.5×10^{17} m^{-3}. Coarse mode particles are present in concentrations of 9.4×10^9 m^{-3}. Thus, even though the coarse mode contains 95% of the aerosol mass, the coarse mode contains less than 0.0000013% of total aerosol number. This difference encourages nuclei–nuclei coagulation even though $\beta(v, v')$ is a minimum when $v = v'$ (Eq. (9)). Thus, it would seem that the use of large ash particles to scavenge submicron trace metal particles through coagulation is not possible in the times available.

5.3. Condensation

Heterogeneous condensation does not affect the aerosol number concentration, but allows for mass (or volume) addition through growth of existing particles. Heterogeneous condensation of a species onto the surface of an existing aerosol can be described by the combination of a source term or growth law, $I(v)$, which describes the size dependent driving force for mass addition through condensation for particles of size v (including chemical and physical properties of the system) times the number density of particles of size v, $n(v, x, t)$, at position x, and time t:

$$R_{\mathrm{cond}} = \frac{\partial}{\partial v}[I(v)n(v, x, t)] \quad (1/\mathrm{m}^3\,\mathrm{s}), \tag{10}$$

where $I(v) = \mathrm{d}v/\mathrm{d}t$ has units of m^3/s. Growth laws for diffusion, molecular bombardment, surface reaction, and droplet phase reaction are given by Friedlander [30]. For example, as with coagulation, in the continuum regime ($Kn \ll 1$), growth is limited by the rate of transport of a condensing species to the particle surface. The rate of diffusional condensation of a species i on a single particle of (constant) size, d_p, for the continuum range, is derived from Fick's law in a quiescent medium as

$$F_i(d_\mathrm{p}) = \frac{2\pi d_\mathrm{p} D_\mathrm{im}}{RT}(P_i^\infty - P_i^\mathrm{sat}) \quad \text{when } Kn \ll 1 \quad (\mathrm{g\,mol/s}), \tag{11}$$

where D_im is the pseudo binary diffusion coefficient, and P_i^∞ and P_i^sat are the condensing species vapor pressures far from and near the particle surface, respectively. Depending on the particle size and the nature of the condensing species, P_i^sat may be influenced by the Kelvin effect which results in an increase in the equilibrium vapor pressure inside capillaries and over curved, compared to flat, (exterior) surfaces, and the solute effect, whereby mixtures in solution tend to lower the individual equilibrium vapor pressures compared to pure species. The product of $F_i(d_\mathrm{p})$ and (M_{wi}/ρ_i) yields the growth law $I(v)$ in the appropriate units of m^3/s, rather than of g mol/s.

The mass fraction on an ash particle of a condensed metals species, $W_i(d_\mathrm{p})$, is given by the mass condensed (in time, t) on a particle of size d_p, divided by the particle mass:

$$W_i(d_\mathrm{p}) = \frac{M_{wi}\int_0^t F_i(d_\mathrm{p})\mathrm{d}t}{\frac{1}{6}\pi\rho_\mathrm{p} d_\mathrm{p}^3}. \tag{12}$$

Different condensation mechanisms will yield different dependencies of $F(d_\mathrm{p})$ on d_p. In the cases that follow, it is assumed that d_p does not change appreciably with time (thin film approximation). Continuum film diffusion (Eq. 11, based on Nusselt number = 2) yields $F(d_\mathrm{p}) \sim d_\mathrm{p}$, thus

$$W_i(d_\mathrm{p}) \sim 1/d_\mathrm{p}^2 \quad \text{when } Kn \ll 1, \tag{13}$$

while free molecular film diffusion (mass transfer coefficient independent of d_p) can be shown to yield $F(d_\mathrm{p}) \sim d_\mathrm{p}^2$, and thus

$$W_i(d_\mathrm{p}) \sim 1/d_\mathrm{p} \quad \text{when } Kn \gg 1. \tag{14}$$

Species i may also react at the surface of a particle of diameter, d_p. The reaction rate at the surface per unit area, R_i, is given by

$$R_i = \frac{k_\mathrm{r}}{RT} P_i^\mathrm{s} \quad (\mathrm{g\,mol/m^2\,s}), \tag{15}$$

where k_r(m/s) is the surface reaction rate coefficient and P_i^s is the partial pressure of species i at the surface. Note that P_i^s may be much less than P_i^sat, allowing this process to occur at temperatures higher than the dewpoint. Considering both continuum diffusion and surface reaction, the flow of species i to the surface is given by

$$F_i(d_p) = \frac{\pi d_p^2}{RT}\left(\frac{1}{1/k_r + d_p/2D_{im}}\right)P_i^\infty \quad (\text{g mol/s}) \tag{16}$$

which reduces to Eq. 11 for $k_r \gg 2\ D_{im}/d_p$ (stagnant film diffusion controlled regime), and consequently, a $1/d_p^2$ dependence for $W_i(d_p)$. Under external surface reaction controlled conditions ($k_r \ll 2\ D_{im}/d_p$):

$$F_i(d_p) = \frac{k_r \pi d_p^2}{RT} P_i^\infty \quad (\text{g mol/s}) \tag{17}$$

leading to

$$W_i(d_p) \sim 1/d_p. \tag{18}$$

A $1/d_p$ dependence is also true if the reaction occurs within a porous particle, but is pore diffusion controlled. There is no particle size dependence (no enrichment on small particles) when the process is reaction controlled within the particle.

Physical condensation mechanisms (continuum and free molecular) occur when the temperature is below the metal vapor dewpoint, (neglecting the Kelvin effect, which allows condensation above the dewpoint). Chemical reaction can occur at any temperature far above the dewpoint, and this facet is especially relevant to trace metals in coal, where trace metal concentrations are very low, and dewpoints may also be quite low.

Condensation and surface reaction mechanisms: experimental results

The theory presented above suggests that different condensation mechanisms can lead to different dependencies of metal concentration with respect to particle size. Fig. 8, compiled from data published by Neville and Sarofim [37] and Haynes et al. [38], depicts, for sodium in coal fly ash, a $1/d_p$ dependence in the free molecular regime and a $1/d_p^2$ dependence in the continuum regime, and these data are completely consistent with physical condensation and/or film diffusion controlled reaction, with transport controlled by free molecular and continuum diffusion, respectively. Note that the sodium enrichment data with the $1/d_p$ dependence are for particles with diameters less than the mean free path of the gas molecules (approximately 0.1 μm) while those with the $1/d_p^2$ dependence are for particles much larger than the mean free path. Gallagher et al. [10] found that the slope of the $1/d_p^2$ dependence in the continuum regime decreased with increasing temperature. Neither the larger particles ($d_p > 4$ μm) nor the very small particles ($d_p < 0.4$ μm) followed a $1/d_p^2$ dependence, probably because significant amounts of sodium were present inside, not merely at the surface of, particles at both size extremes.

The arsenic data of Haynes et al. [38] are especially significant, showing a $1/d_p$ dependence even for larger particles lying in the continuum transport regime. Arsenic enrichment, therefore does not occur through physical condensation. Rather, the data suggest a (slow) external surface reaction (or pore diffusion) controlled process.

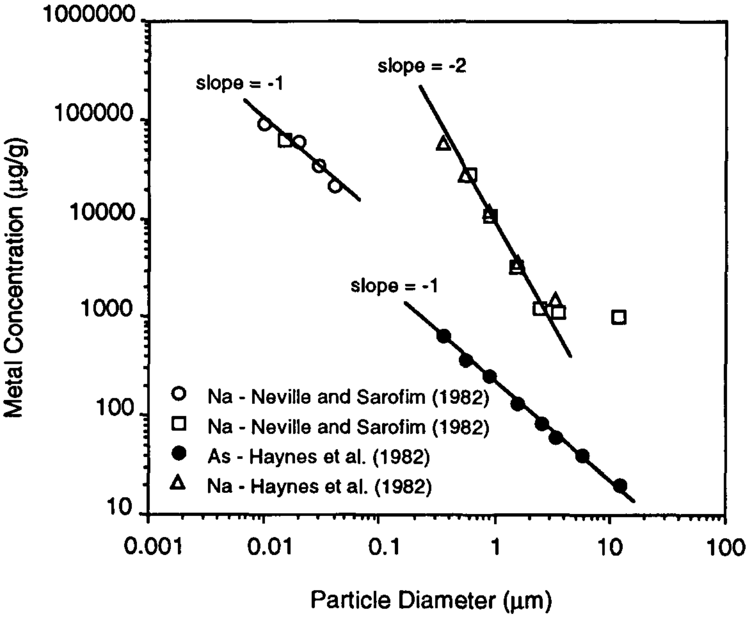

Fig. 8. The dependence of sodium and arsenic on coal fly ash particle size, showing $1/d_p$ and $1/d_p^2$ dependencies (adapted from Neville and Sarofim [37] and Haynes et al. [38]).

A reactive scavenging process for arsenic is consistent with the very low concentrations of arsenic both in the gas phase and in the reacted particles. The temperature of the arsenic vapor was above its dewpoint (without reaction). A probable reactive sorbent was a calcium compound, since, as shown by the equilibrium results in Fig. 3, solid $Ca_3(AsO_4)_2$ can tie up and precipitate the arsenic at high temperatures, if excessive sulfur (compared to calcium) is not present. Similar reactions may occur between other trace metals and existing fly ash particles [38]. Scotto et al. [39] and Uberoi and Shadman [40, 41] have shown similar reactions between lead and aluminosilicates.

The relative importance of film condensation ($1/d_p^2$ dependence) versus reactive scavenging ($1/d_p$ dependence) is not universally agreed upon. Biermann and Ondov [42] suggested that, for coal, a $1/d_p^2$ dependence for arsenic, selenium, and tungsten was superior to a $1/d_p$ dependence, over a particle size range from 0.1–10 µm, although both correlations coincided for $d_p > 0.8$ µm. Conversely, Davison et al. [43] and Haynes et al. [38] strongly suggest that many trace metals (arsenic, nickel, and cadmium in Davison's study and arsenic, antimony, potassium, manganese, vanadium, and tungsten in Haynes' study) follow a $1/d_p$ dependence over particle sizes 0.4 µm $< d_p <$ 10 µm (i.e., the continuum range). This may have a significant positive bearing on both the potential capture of trace metals in the vapor phase and the potential leachability of trace metals in the collected ash. In summary, the data show that surface condensation can account for the sodium mass contribution to the mid particle size range, although very small particles may consist of a sodium fume, and large particles may contain sodium distributed throughout. Several trace metals on the other hand appear to be reactively scavenged or chemisorbed on existing particles, although the generality of this hypothesis, and its relationship to the presence of other species in coal, remains to be established.

6. Conclusions

Trace metal transformation mechanisms during the combustion of pulverized coal control the metal speciation in the effluent and the subsequent impact of trace metals on the environment. Equilibrium considerations can provide a valuable guide on the propensity of trace metals to vaporize or condense in coal combustion flue gases. Experimental data from a practical combustor, into which individual metals were introduced in an idealized form, supported equilibrium predictions, especially the role of chlorine. Chlorine can strongly enhance the vaporization of many trace metals.

Coagulation processes can be modeled using existing computational tools, and these models agree well with experimental data. Coagulation, however, does not allow particles in the submicron mode (approximately 5% of the total mass) to be scavenged by the larger ash particles. Rather, the available data, with some exceptions, show that arsenic, and many other trace metals, are captured by existing ash particles via an external surface reaction controlled process. In contrast to physical condensation, this reactive process allows interactions between metal vapor and supermicron particles at temperatures above the metal vapor dewpoint, and leads to enrichment that depends inversely on particle diameter itself, rather than on the inverse of the square of particle diameter. Although more research is needed, one might currently speculate that, through this form of reactive scavenging, one can potentially use the high-temperature combustion process to convert trace (toxic) metals into a more easily controlled, unleachable, environmentally benign form.

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References

[1] Resource conservation and recovery act, Subtitle C, Sections 3001–3013, 42 N.S.C., Sections 6921–6934, 1976 and Supplement IV, 1980, amended 1986.

[2] Clean Air Act Amendments, Public Law 101–549, 104 Stat. 2399–2712, Nov. 15 1990.

[3] Markowski, G.R., Ensor, D.S., Hooper, R.G. and Carr, R.C., 1980. A submicron aerosol mode in flue gas from a pulverized coal utility boiler. Environ. Sci. Technol., 14(11): 1400–1402.

[4] Linak, W.P. and Wendt, J.O.L., 1993. Toxic metal emission from incineration: mechanisms and control. Prog. Energy Combust. Sci., 19: 145–185.

[5] Finkelman, R.B., 1993. Mode of occurrence of hazardous elements in coal: level of confidence. Trace Element Transformations in Coal-Fired Power Systems Workshop, Scottsdale, AZ, April 19–22, 1993.

[6] Neville, M. and Sarofim, A.F., 1985. The fate of sodium during pulverized coal combustion. Fuel, 64: 384–390.

[7] Mims, C.A., Neville, M., Quann, R.J., House, K. and Sarofim, A.F., 1980. Laboratory studies of mineral matter vaporization during coal combustion. AIChE Symp. Ser., 76(201): 188–194.

[8] Wibberly, L.J. and Wall, T.F., 1982. Alkali-ash reactions and deposit formation in pulverized-coal-fired boilers: experimental aspects of sodium silicate formation and the formation of deposits. Fuel, 61: 93–99.

[9] Linder, E.R. and Wall, T.F., 1990. Sodium ash reactions during combustion of pulverized coal, Proceedings of the 23rd Combustion (International) Symposium, 1313–1321, Combustion Institute, Pittsburgh, PA.

[10] Gallagher, N.B., Bool, L.E., Wendt, J.O.L. and Peterson, T.W., 1990. Alkali metal partitioning in ash from pulverized coal combustion. Combust. Sci. Technol., 74: 211–221.

[11] Gallagher, N., Peterson, T.W. and Wendt, J.O.L., 1991. Alkali/silicate interactions during pulverized coal combustion. Proceedings of the 201st ACS National Meeting Preprints, 36(1): 181–190.

[12] Gallagher, N.B., Bool, L.E., Wendt, J.O.L. and Peterson, T.W., 1991. Alkali/silicate interactions during pulverized coal combustion. Am. Chem. Soc., Div. of Fuel Chem., Atlanta, GA.

[13] Helble, J.J., Srinivasachar, S. and Boni, A.A., 1990. Factors influencing the transformation of minerals during pulverized coal combustion. Prog. Energy Combust. Sci., 16: 267–279.

[14] Gallagher, N.B., 1992. Alkali metal partitioning in a pulverized coal combustion environment, Ph.D. Dissertation, University of Arizona, Tucson, AZ.

[15] Gordon, S. and McBride, B.J., 1986. Computer program for calculation of complex chemical equilibrium compositions, rocket performance, incident and reflected shocks, and Chapman–Jouguet detonations. NASA SP-273, Interim Revision.

[16] Queneau, P.B., May, L.D. and Cregar, D.E., 1991. Application of slag technology to recycling of solid wastes, 1991 Incineration Conference, Knoxville, TN, 69–85.

[17] Helble, J.J., Srinivasachar, S., Wilemski, G., Boni, A.A., Kang, S.G., Sarofim, A.F., Graham, K.A., Beer, J.M., Peterson, T.W., Wendt, J.O.L., Gallagher, N.B., Bool, L., Huggins, F.E., Huffman, G.P., Shah, N. and Shah, A., 1992. Transformations of inorganic coal constituents in combustion systems. US DOE final report, contract DE-AC22-86PC90751.

[18] DeVito, M.S., Rosendale, L.W. and Conrad, V.B., Comparison of trace element contents of raw and clean commercial coals, Trace Element Transformations in Coal-Fired Power Systems Workshop, Scottsdale, AZ, April 19–22, 1993.

[19] Eddings, E.G. and Lighty, J.S., 1992. Fundamental studies of metal behavior during solids incineration. Combust. Sci. Technol., 85, 375–385.

[20] Linak, W.P., Srivastava, R.K. and Wendt, J.O.L., 1993. Metal aerosol formation in a laboratory swirl flame incinerator. Combust. Sci. Technol., submitted.

[21] Beer, J.M. and Chigier, N.A., 1983. Combustion Aerodynamics, Robert E. Krieger Publishing Co., Malabar, FL.

[22] Scotto, M.A., 1992. Mechanisms Governing the Abatement of Metal Emissions from Waste Incineration. Ph.D. Dissertation, University of Arizona, Tucson, AZ.

[23] Frenkel, J., 1955. Kinetic theory of liquids, Dover Press, New York.

[24] Senior, C.L. and Flagan, R.C., 1982. Ash vaporization and condensation during combustion of a suspended coal particle. Aerosol Sci. Technol., 1: 371–383.

[25] Helble, J., Neville, M. and Sarofim, A.F., 1986. Aggregate formation from vaporized ash during pulverized coal combustion, Proceedings of the 21st Combustion (International) Symposium, Combustion Institute, Pittsburgh, PA, 411–417.

[26] McNallan, M.J., Yurek, G.J. and Elliott, J.F., 1981. The formation of inorganic particulates by homogeneous nucleation in gases produced by the combustion of coal. Combust. & Flame, 42: 45–60.

[27] Scotto, M.V., Bassham, E.A., Wendt, J.O.L. and Peterson, T.W., 1988. Quench-induced nucleation of ash constituents during combustion of pulverized coal in a laboratory furnace, Proceedings of the 22nd Combustion (International) Symposium, Combustion Institute, Pittsburgh, PA, 239–247.

[28] Taylor, D.D. and Flagan, R.C., 1982. The influence of combustor operation on fine particles from coal combustion. Aerosol Sci. Technol., 1: 103–117.

[29] Lin, W.Y., Sethi, V. and Biswas, P., 1992. Multicomponent aerosol dynamics of the Pb–O_2 system in a bench scale flame incinerator. Aerosol Sci Technol., 17: 119–133.

[30] Friedlander, S.K., 1977. Smoke dust and haze — fundamentals of aerosol behavior, Wiley, New York.

[31] Smoulochowski, M., 1917. Versuch einer mathematischen theorie der koagulationskinetik kolloider losungen. Z. Phys. Chem., 92: 129–168.

[32] Fuchs, N.A., 1964. C.N. Davies, (Ed.) In: The Mechanics of Aerosols, Pergamon Press, Oxford, UK.

[33] Gelbard, F. and Seinfeld, J.H., 1980. Simulation of multicomponent aerosol dynamics. J. Colloid Interface Sci., 78(2): 485–501.

[34] U.S. EPA, 1988. Compilation of air pollution emission factors, vol. 1: stationary point and area sources, AP-42 (NTIS PB89-128631), Supplement B.

[35] Linak, W.P. and Peterson, T.W., 1986. Mechanisms governing the composition and size distribution of ash aerosol in a laboratory pulverized coal combustor, Proceedings of the 21st Combustion (International) Symposium, Combustion Institute, Pittsburgh, PA, 399–410.

[36] Matsoukas, T. and Friedlander, S.K., 1991. Dynamics of aerosol agglomerate formation. J. Colloid Interface. Sci., 146(2): 495–506.

[37] Neville, M. and Sarofim, A.F., 1982. The stratified composition of inorganic submicron particles produced during coal combustion, Proceedings of the 19th Combustion (International) Symposium, Combustion Institute, Pittsburgh, PA, 1441–1449.

[38] Haynes, B.S., Neville, M., Quann, R.J. and Sarofim, A.F., 1982. Factors governing the surface enrichment of fly ash in volatile trace species. J. Colloid Interface Sci., 87(1): 266–278.

[39] Scotto, M.A., Peterson, T.W. and Wendt, J.O.L., 1992. Hazardous waste incineration: the in-situ capture of lead by sorbents in a laboratory down-flow combustor, Proceedings of the 24th Combustion (International) Symposium, Combustion Institute, Pittsburgh, PA, 1109–1118.

[40] Uberoi, M. and Shadman, F., 1990. Sorbents for the removal of lead compounds from hot flue gases. AIChE J., 36(2): 307–309.

[41] Uberoi, M. and Shadman, F., 1991. High-temperature removal of cadmium compounds using sorbents. Environ. Sci. Technol., 25(7): 1285–1289.

[42] Biermann, A.H. and Ondov, J.M., 1980. Application of surface-deposition models to size-fractionated coal fly ash. Atmos. Environ., 14: 289–295.

[43] Davison, R.L., Natusch, D.F.S., Wallace, J.R. and Evans, C.A. Jr., 1974. Trace elements in fly ash dependence of concentration on particle size. Environ. Sci. Technol., 8(13): 1107–1113.

[44] Coles, D.G., Ragaini, R.C. and Ondov, J.M., 1978. Behavior of natural radionuclides in western coal-fired power plants. Environ. Sci. Technol., 12(4): 442–446.

[45] Damle A.S., Ensor, D.S. and Ranade, M.B., 1982. Coal combustion aerosol formation mechanisms: a review. Aerosol Sci. Technol., 1: 119–133.

[46] Desrosiers, R.E., Riehl, J.W., Ulrich, G.D. and Chiu, A.S., 1979. Submicron fly-ash formation in coal-fired boilers, Proceedings of the 17th Combustion (International) Symposium, Combustion Institute, Pittsburgh, PA, 1395–1403.

[47] Flagan, R.C. and Taylor, D.D., 1981. Laboratory studies of submicron particles from coal combustion, Proceedings of the 18th Combustion (International) Symposium, Combustion Institute, Pittsburgh, PA, 1227–1237.

[48] Gladney, E.S., Small, J.A., Gorden, G.E. and Zoller, W.H., 1976. Composition and size distribution of in-stack particulate material at a coal-fired power plant. Atmos. Environ., 10: 1071–1077.

[49] Kaakinen, J.W., Jorden, R.M., Lawasani, M.H. and West, R.E., 1975. Trace element behavior in coal-fired power plant. Environ. Sci. Technol., 9(9): 862–869.

[50] Kauppinen, E.I. and Pakkanen, T.A., 1990. Coal combustion aerosols: a field study. Environ. Sci. Technol., 24(12): 1811–1818.

[51] Klein, D.H., Andren, A.W., Carter, J.A., Emery, J.F., Feldman, C., Fulkerson, W., Lyon, W.S., Ogle, J.C., Talmi, Y., VanHook, R.I. and Bolton, N., 1975. Pathways of thirty-seven trace elements through coal-fired power plant. Environ. Sci. Technol., 9(10): 973–979.

[52] Neville, M., McCarthy, J.F. and Sarofim, A.F., 1983. Size fractionation of submicrometer coal combustion aerosol for chemical analysis. Atmos. Environ., 17(12): 2599–2604.

[53] Ondov, J.M., Ragaini, R.C. and Biermann, A.H., 1978. Elemental particle-size emissions from coal-fired power plants: use of an inertial cascade impactor. Atmos. Environ., 12: 1175–1185.

[54] Ondov, J.M., Ragaini, R.C. and Biermann, A.H., 1979. Elemental emissions from a coal-fired power plant. Comparison of a venturi wet scrubber system with a cold-side electrostatic precipitator. Environ. Sci. Technol., 13(5): 598–607.

[55] Quann, R.J. and Sarofim, A.F., 1982. Vaporization of refractory oxides during pulverized coal combustion, Proceedings of the 19th Combustion (International) Symposium, Combustion Institute, Pittsburgh, PA, 1429–1440.

[56] Quann, R.J., Neville, M., Janghorbani, M., Mims, C.A. and Sarofim, A.F., 1982. Mineral matter and trace-element vaporization in a laboratory-pulverized coal combustion system. Environ. Sci. Technol., 16(11): 776–781.

[57] Shendrikar, A.D., Ensor, D.S., Cowen, S.J., Woffinden, G.J. and McElroy, M.W., 1983. Size-dependent penetration of trace elements through a utility baghouse. Atmos. Environ., 17(8): 1411–1421.

[58] Smith, R.D., Campbell, J.A. and Nielson, K.K., 1979. Characterization and formation of submicron particles in coal-fired plants. Atmos. Environ., 13: 607–617.

[59] Smith, R.D., Campbell, J.A. and Nielson, K.K., 1980. Volatility of fly ash and coal. Fuel, 59: 661–665.

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2. D. Grosjean and S. K. Friedlander, *JAPCA*, **25**, 1038 (1975).
3. R. C. Flagan and S. K. Friedlander, "Particle Formation in Pulverized Coal Combustion—A Review," Chap. 2 this volume.
4. S. K. Friedlander, *Smoke, Dust and Haze: Fundamentals of Aerosol Behavior*, Wiley-Interscience, New York, 1977.
5. C. T. R. Wilson, "On the Cloud Method of Making Visible Ions and the Tracks on Ionizing Particles," in *Nobel Lectures in Physics 1922–1941*, 1927.
6. J. Frenkel, *Kinetic Theory of Liquids*, Dover, 1955.
7. B. J. Mason, *The Physics of Clouds*, Clarendon, Oxford, 1971.
8. P. P. Wegener and A. A. Pouring, *Phys. Fluids*, 7, 352 (1964).
9. R. H. Heist and H. Reiss, *J. Chem. Phys*., **59**, 665 (1971).
10. P. T. Roberts and S. K. Friedlander, *Environ. Health Perspect*., **10**, 103 (1975).
11. S. P. Sander and J. H. Seinfeld, *Environ. Sci. Technol*., **10**, 1114 (1976).
12. J. G. Calvert, "Interactions of Air Pollutants," in *Proceedings of the Conference on Health Effects of Air Pollutants*, U.S. Government Printing Office No. 93-15, 1973.
13. H. Reiss, *J. Chem. Phys*., **18**, 840 (1950).
14. D. Grosjean, personal communication, 1975.
15. C. S. Kiang and D. Stauffer, *Faraday Symp. Chem. Soc*., No. 7, 29 (1973).
16. P. Mirabel and J. L. Katz, *J. Chem. Phys*., **60**, 1138 (1974).
17. N. A. Fuchs and A. G. Sutugin, "High-Dispersed Aerosols," in G. M. Hidy and J. R. Brocks, Eds., *Topics in Current Aerosol Research*, Pergamon, New York, 1971.
18. P. H. McMurry, "On the Relationship between Aerosol Dynamics and the Rate of Gas-to-Particle Conversion," Ph.D Thesis in Environmental Engineering Science, California Institute of Technology, Pasadena, Calif., May 2, 1975.
19. W. D. Scott and P. V. Hobbs, *J. Atmos. Sci*., **24**, 54 (1967).
20. C. E. Junge and T. G. Ryan, *Q. J. R. Meteorolol. Soc*., **84**, 46 (1958).
21. J. Freiberg, *Environ. Sci. Technol*., **8**, 731 (1974).
22. K. G. Denbigh, *The Principles of Chemical Equilibrium*, 2nd ed., Cambridge University Press, New York, 1966.
23. J. R. Brock, *Atmos. Environ*., New York, 5, 833 (1971).
24. J. L. Katz, C. J. Scoppa, N. G. Kumar, and P. Mirabel, *J. Chem. Phys*., **62**, 448 (1975).
25. S. L. Heisler and S. K. Friedlander, *Atmos. Environ*. **11**, 185 (1977).

CHAPTER 2 PARTICLE FORMATION IN PULVERIZED COAL COMBUSTION—A REVIEW

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1. NOMENCLATURE

C_i	concentration, molecules cm^{-3}
$\bar{C}$	concentration in fly ash
C_0, C_s	coefficients
d, d_p	particle diameter
D	diffusivity
F	diffusion flux to particle surface
I_1, I_2, I_3	moments of free molecule regime self-preserving size distribution
I_D	integral for diffusion to surfaces of large particles
K	coefficient, defined by Eq. 12
Kn	Knudsen number
k	Boltzmann constant
M	total mass per unit volume
m	mass of gas molecule
$\tilde{N}(t)$	total number of particles per unit mass at time t
$n(v,t)$	particle size distribution function, particles cm^{-3}cm^{-3}
$n(d_p)$	particle size distribution function, particles cm^{-3}cm^{-3}
$\tilde{n}(v,t)$	particle size distribution function, particles cm^{-3}cm^{-3}
P	pressure
p	number of ash particles produced per coal particle
R	gas constant
T	temperature
t	time
$\mathbf{u}$	gas velocity
$\tilde{V}$	total aerosol volume, cm^{3}g^{-1}
v	particle volume
α	mass fraction ash in coal
α_c	accommodation coefficient
α_v	volume fraction ash in coal
$\beta(v,v')$	collision parameter
η	dimensionless particle volume
λ	mean free path
τ	time parameter, defined by Eq. 12
$\Psi(\eta)$	dimensionless distribution function

Subscripts

a	ash
c	coal
l	large particles produced by breakup
r	particle
s	small particles produced by homogeneous nucleation

2. INTRODUCTION

Particulate emissions from coal combustion sources were among the first forms of air pollution to be controlled. The opacity of stack plumes and the total mass of particulate matter emitted have been significantly reduced through improvements in combustor operation and the use of gas cleaning devices such as electrical precipitators. In spite of these improvements, coal combustion is still a major source of particulate emissions. Moreover, electrical precipitators may show a minimum in collection efficiency for particles in the 0.1–1.0 μm size range [1]. Such particles have longer atmospheric residence times and greater effects on health and visibility than would an equal mass of larger particles.

Coal combustion is an important source of heavy metals in the environment [2–9]. Many species, including cadmium, arsenic, selenium, lead, nitrogen, zinc, and antimony, are present in the fly ash particles emitted by coal fired power plants and in ambient urban aerosols in concentrations much larger than their natural crustal abundance [10] as shown in Fig. 1. Recent studies have shown that the concentrations of several trace species in fly ash increase with decreasing particle size [11–17]. Few measurements of ash size distributions have been made using techniques suitable for particles smaller than about 5 μm diameter [18]. Studies of the fractional efficiency of particle collection equipment have recently provided some more complete size distribution data [1, 19, 20]. Data on the composition-size distribution have been obtained for few sources and have not been extended far into the submicron size range.

The composition-size distributions of particles emitted by coal combustion sources are influenced by furnace design and operating conditions. A wide variety of coal combustion equipment is currently in use. New designs are being developed because of recent constraints on emissions of gaseous and particulate pollutants and on fuel availability. Electrostatic precipitator performance may be seriously impaired when a low sulfur coal is substituted for a coal with a higher sulfur content and correspondingly lower resistivity ash. Fabric filters may replace electrical precipitators for particle collection where low sulfur coal is burned. Some combustion modifications may change the quantities of fine particles in the flue gases. To anticipate the future requirements for particulate emission control and to evaluate the environmental impact of increased coal use, it is necessary to know the characteristics of the aerosol entering the gas cleaning devices. An examination of the mechanism of particle formation during coal combustion may provide much of the necessary information.

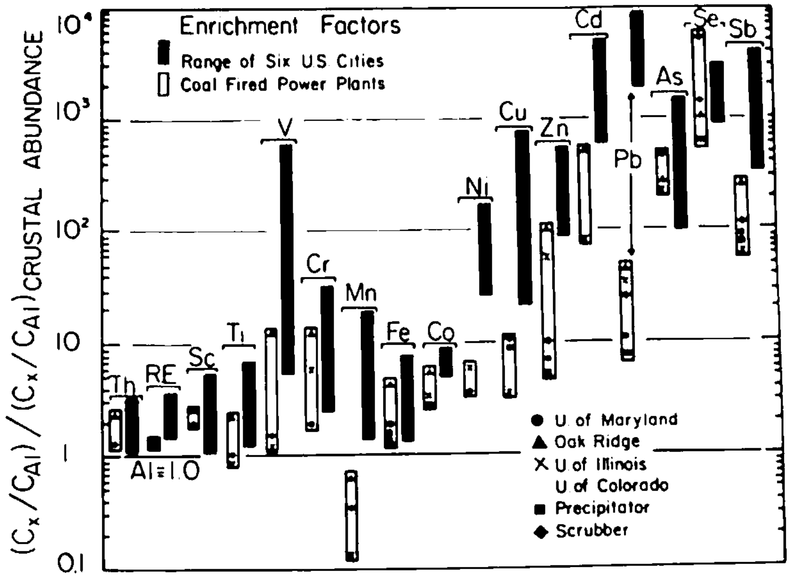

Fig. 1. Enrichment factors for several elements on ambient particles collected in several U.S. cities and on particles collected downstream of gas cleaning devices on coal fired power plants. Enrichment is calculated relative to the natural crustal abundance of the elements. (Data from Ref. 10.)

Emissions from coal combustion may include several types of materials, such as char, soot, fly ash, and droplets containing sulfuric acid. Improvements in combustion conditions have, in recent years, reduced the amount of partially burned coal char emitted from utility boilers. The combustible content of the particulate emissions from large sources generally accounts for only a small fraction of the total mass of emissions [11, 21]. Soot is formed by the condensation and subsequent pyrolysis of high molecular weight hydrocarbons [22, 23]. Fly ash is formed from the mineral matter in the coal. During combustion the mineral matter undergoes chemical transformations to form ash and, if temperatures are sufficiently high, the ash fuses to form spherical particles [24–34]. Some ash may be vaporized in the high temperature flame region and later condense homogeneously to form large numbers of very small fly ash particles [35–37]. Submicron fly ash particles may also be produced by the bursting of bubbles as gases are evolved within molten ash particles [28, 29].

The presence of sulfur trioxide (SO_3) in the flue gases of coal fired boilers results in the formation of alkali metal sulfates or sulfuric acid when it condenses [37]. The homogeneous oxidation of sulfur to form SO_2 is fairly well understood [38]. Less is known about the mechanism of SO_3 formation. Generally about 1% of the sulfur is present in the flue gases as SO_3 [38]. As the flue gases cool, this SO_3 may condense with water vapor to form sulfuric acid droplets. Stack temperatures are usually maintained above the dew point of the SO_3–H_2O mixture to prevent acid condensation within the stack.

Studies of the occurrence of deposits in boilers [37] and microscopic examinations of fly ash particles [24–34] provide the basis for a preliminary analysis of fly ash formation and identify some of the important processes that occur. The present study is restricted to the examination of particle formation in pulverized coal fired systems. This is the predominant method of coal combustion for electric power generation. Moreover, most of the available data on particle formation and emissions have been obtained on pulverized fuel equipment.

3. PULVERIZED COAL COMBUSTION

Pulverized coal fired boilers burn coal that has been crushed and ground to a fine powder [39, 40]. The mass mean diameter of the coal particles is typically in the range of 30 to 70 μm. The distribution of coal sizes is broad. A coal powder with a 50 μm mass mean diameter may have 10% of the mass smaller than 10 μm and 10% larger than 100 μm. The few reported measurements of coal size distributions indicate that the distribution varies significantly from one power plant to another [41]. Coal burned in a suspension at 1800–2500°K must remain at high temperature long enough for the largest particles to burn completely. About 1 sec is required to burn a 200 μm diameter coal particle. Smaller particles burn much more rapidly.

Pulverized coal fired boilers are generally large; units producing 500 MW electrical output are common. Many furnaces larger than about 600 MW are divided into two combustor chambers. Pulverized coal is injected into the furnace with about one-fifth of the total air flow, the primary air, through a number of burners [39]. A 500 MW boiler, illustrated in Fig. 2, may have 30 or more burners arranged in one of a number of possible patterns in the furnace walls. Preheated air is introduced into the furnace through air registers coaxial with the burners. In the furnace the coal is heated by thermal radiation and by mixing with hot combustion products, igniting the coal particles. The temperatures of the burning coal particles and the gas surrounding them rise rapidly. Mixing in the furnace is relatively slow. As a result, the temperature and composition of the combustion gases are far from uniform. Although peak temperatures may be as high as 2500°K, some coal particles may be subjected to much lower combustion temperatures. The variability in time–temperature history of the coal particles may be responsible for much of the diversity of ash characteristics observed in the emissions from a combustion system. A complete representation of the kinetic processes occurring in a furnace would require a statistical description of the composition and temperature fluctuations and the residence time distribution in the boiler [42, 43].

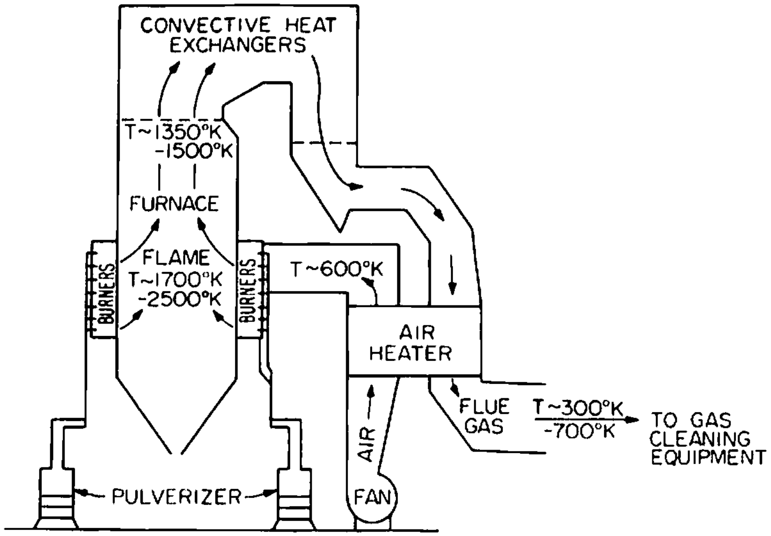

Fig. 2. Pulverized coal fired boiler.

In the furnace the temperature of the combustion products is reduced by the combined effects of radiation and convective heat transfer. About one-half of the heat released during combustion is transferred to the water tube walls of the furnace before the combustion products enter the convective heat exchangers. The temperature at the furnace outlet is limited to about 1350–1500°K in order to prevent damage to the superheater tubes. A long residence time of the combustion gases in the boiler, about 1 to 2 sec, is necessary to assure both complete combustion and adequate heat transfer upstream of the superheaters.

A typical 500 MW pulverized coal fired electric power plant has a furnace about 30 m high with a cross-sectional area of about 260 m^2 [44].

Operating at about 35% thermal efficiency, this unit requires about 1430 MW of thermal input, for instance, approximately 48 Kg sec^{-1} (170 T hr^{-1}) of a bituminous coal with a lower heating value of 3×10^7J kg^{-1} (12900 Btu lb^{-1}). Burning a coal containing 10% ash, this unit produces about 4.8 kg sec^{-1} (17 T hr^{-1}) of ash. If all the ash were carried out of the furnace in the flue gases, the aerosol mass loading would be about 9 g m^{-3} at standard conditions.

Pulverized coal is burned in a variety of types of combustors. The peak temperatures and the amount of ash impacting on the boiler walls are strongly influenced by the furnace design. Some units, designed to achieve rapid mixing of fuel and air, result in high combustion intensities and thus high flame temperatures. Boilers in which fuel and air mix relatively slowly have lower flame temperatures. Because nitric oxide emissions increase at high temperature, the latter designs are being favored for new installations. Cyclone burners were designed to remove most of the ash from the flue gases before they enter the superheaters where deposits cause reliability problems. As much as 80–90% of the ash is impacted on the burner of a cyclone fired furnace [45]. A large fraction of the ash, 60–100%, leaves the combustion chambers of most other types of boilers with the flue gases.

After the combustion products leave the combustion chamber, they enter a series of heat exchangers where heat is transferred from the hot gases to the heat transfer surfaces primarily by convection. In this region the combustion products are cooled from the boiler outlet temperature to the inlet temperature of the emission control equipment, 300–700°K, in a residence time of several seconds. The formation of deposits in this region and the corrosion that accompanies the deposits are major causes of boiler failure. The fraction of the ash deposited in this region is probably small.

4. MINERAL MATTER IN COAL

The ash forming constituents of coal occur in two main classes. Inherent mineral matter, which seldom exceeds 2% of the coal mass, is derived from the original plant substance. Extraneous mineral matter is inorganic material that was mixed with the plant substance as the coal was formed or during mining operations [37].

The extraneous mineral matter may be present as very fine inclusions dispersed throughout the coal volume, or it may be made up of large, distinct structures. The mineral inclusions are generally small compared to the mean coal particle size. Padia [33] has reported Rosin–Rammler distributions fit to mineral size distributions measured after the carbon matrix of coal was oxidized in a low temperature ($T \approx 425$°K) oxygen plasma. The measured volume mean diameters were 1.7 and 2 μm for a lignite and a bituminous coal, respectively. From the size distribution parameters reported, the number mean diameter of the lignite inclusions is about 1 μm. It is not possible to determine the number mean diameter using the parameters given for the inclusions in the bituminous coal.

The mineral matter in coal consists primarily of kaolinite ($Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$), pyrites ($FeS_2$), and calcite ($CaCO_3$) [37, 46]. The major elements in the coal minerals are those found in silicate rocks, silicon, aluminum, calcium, magnesium, iron, sulfur, sodium, potassium, chlorine, and titanium [47]. The mean concentrations of these major elements and a number of minor and trace species in coal are presented in Table 1.

Table 1. MEAN COMPOSITION FOR 101 COALS[a]

Constituent[b]	Mean		Standard Deviation	Min	Max
As	14.02	PPM	17.70	0.50	93.00
B	102.21	PPM	54.65	5.00	224.00
Be	1.61	PPM	0.82	0.20	4.00
Br	15.42	PPM	5.92	4.00	52.00
Cd	2.52	PPM	7.60	0.10	65.00
Co	9.57	PPM	7.26	1.00	43.00
Cr	13.75	PPM	7.26	4.00	54.00
Cu	15.16	PPM	8.12	5.00	61.00
F	60.94	PPM	20.99	25.00	143.00
Ga	3.12	PPM	1.06	1.10	7.50
Ge	6.59	PPM	6.71	1.00	43.00
Hg	0.20	PPM	0.20	0.02	1.60
Mn	49.40	PPM	40.15	6.00	181.00
Mo	7.54	PPM	5.96	1.00	30.00
Ni	21.07	PPM	12.35	3.00	80.00
P	71.10	PPM	72.81	5.00	400.00
Pb	34.78	PPM	43.69	4.00	218.00
Sb	1.26	PPM	1.32	0.20	8.90
Se	2.08	PPM	1.10	0.45	7.70
Sn	4.79	PPM	6.15	1.00	51.00
V	32.71	PPM	12.03	11.00	78.00
Zn	272.29	PPM	694.23	6.00	5350.00
Zr	72.46	PPM	57.78	8.00	133.00
Al	1.29	%	0.45	0.43	3.04
Ca	0.77	%	0.55	0.05	2.67
Cl	0.14	%	0.14	0.01	0.54
Fe	1.92	%	0.79	0.34	4.32
K	0.16	%	0.06	0.02	0.43
Mg	0.05	%	0.04	0.01	0.25

Table 1. (Continued)

Constituent[b]	Mean		Standard Deviation	Min	Max
Na	0.05	%	0.04	0.00	0.20
Si	2.49	%	0.80	0.58	6.09
Ti	0.07	%	0.02	0.02	0.15
ORS	1.41	%	0.65	0.31	3.09
PYS	1.76	%	0.86	0.06	3.78
SUS	0.10	%	0.19	0.01	1.06
TOS	3.27	%	1.35	0.42	6.47
SXRF	2.91	%	1.24	0.54	5.40
ADL	7.70	%	3.47	1.40	16.70
MOIS	9.05	%	5.05	0.01	20.70
VOL	39.70	%	4.27	18.90	52.70
FIXC	48.82	%	4.95	34.60	65.40
ASH	11.44	%	2.89	2.20	25.80
BTU/LB	12748.91		464.50	11562.00	14362.00
C	70.28	%	3.87	55.23	80.14
H	4.95	%	0.31	4.03	5.79
N	1.30	%	0.22	0.78	1.84
O	8.68	%	2.44	4.15	16.03
HTA	11.41	%	2.95	3.28	25.85
LTA	15.28	%	4.04	3.82	31.70

[a] From Ref. 47, reprinted with permission.

[b] Abbreviations other than standard chemical symbols: organic sufur (ORS), pyritic sulfur (PYS), sulfate sulfur (SUS), total sulfur (TOS), sulfur by X-ray fluorescence (SXRF), air-dry loss (ADL), moisture (MOIS), volatile matter (VOL), fixed carbon (FIXC), high temperature ash (HTA), low temperature ash (LTA).

When coal is heated, the mineral matter undergoes a number of transitions [48]. At temperatures below about 500°K dehydration and changes in mineral forms occur. Pyrite is oxidized at temperatures below about 800°K. Carbonates and sulfates decompose at temperatures in the range 500–1100°K, evolving CO_2, SO_2, and SO_3. Alkali salts, such as chlorides, are volatilized at an appreciable rate when the temperature exceeds about 1350°K. Silica may volatilize at temperatures higher than about 1900°K [33, 35, 36, 49–54], largely because of the reduction of SiO_2 by reaction with carbon to form SiO, which is much more volatile than SiO_2. At temperatures higher than about 2500°K, a condition that is not achieved in conventional pulverized coal combustion but may occur in magnetohydrodynamic generators, appreciable quantities of alumina may also be volatilized. Measurements of the distribution of ash composition as a function of particle size suggest that many minor ash constituents are also vaporized during coal combustion.

The tests that determine the ash content of coals involve the slow combustion of coal at a relatively low temperature, about 1000°K, and determination of the quantity of the residual ash. Since combustion in boilers occurs at much higher temperatures, transitions that do not occur in the standard tests may take place. Some of these changes result in the evolution of considerable quantities of CO_2, SO_2, and SO_3. This decomposition may account for a major fraction of the weight loss of the ash, as is shown in Fig. 3. Nonetheless, a substantial fraction of the ash may be lost through vaporization. As much as 4–8% of the ash was vaporized in Padia's experiments [33].

The tendency of ash to melt when heated has posed problems for engineers since the earliest days of steam generation [37]. When coal is

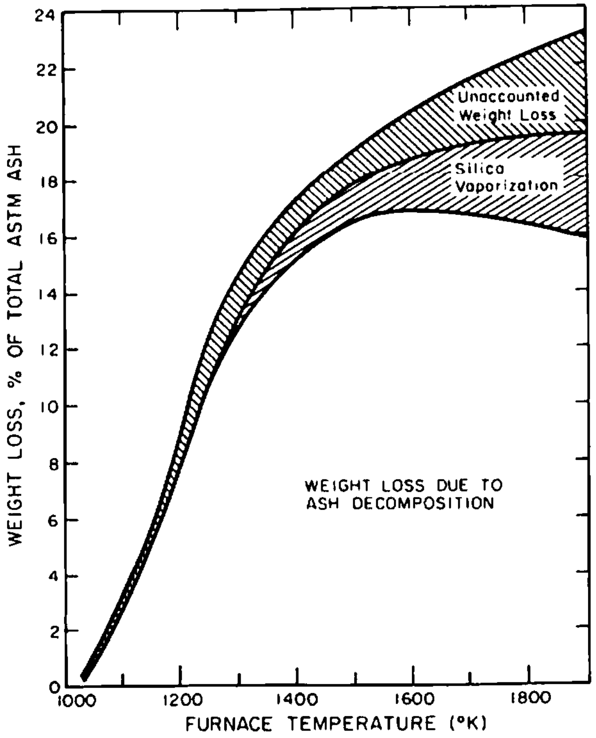

Fig. 3. Loss of ash during fuel lean combustion of 38–45 μm lignite particles in a laminar flow furnace. (From Ref. 33.)

burned in a fuel bed, the ash softens and then may fuse to form clinkers. To determine the relative tendencies of different coals to form clinkers, tests were devised to measure the fusibility of ash. Empirical tests have been developed to determine the initial deformation temperature, the softening temperature, and the fluid temperature [37]. More quantitative information is obtained for some ashes by measuring the viscosity of the ash as a function of temperature. The viscosity of the ash decreases rapidly with increasing temperature and also depends strongly on the composition of the ash. The presence of iron as Fe_2O_3 in the ash results in the ash behaving as a fluid at much lower temperatures than the same ash would behave if the iron were present only in its reduced state, FeO [37]. Other species have similar strong effects on the characteristics.

Examination of fly ash particles reveals that most particles were molten during their formation process. The particles tend to be spherical except where considerable agglomeration has occurred. Since the temperature at which the ash becomes fluid may vary over several hundred degrees, depending on the coal characteristics and whether the combustion environment is oxidizing or reducing, and since the peak temperatures are determined by the combustion conditions, it is expected that combustion conditions may strongly influence the character of the ash emissions.

5. FLY ASH PARTICLE FORMATION

The processes that influence the ash particle formation occur primarily in the final stages of coal particle burnout. Initially, as a coal particle is heated, volatile hydrocarbons originally present in the coal or produced by pyrolysis are vaporized. Some of the mineral matter inherent in the organic structure of the coal may be vaporized during this process. Mercury and other extremely volatile ash constituents may also be vaporized during this early phase of combustion. After the volatile hydrocarbons are vaporized, the residual char burns by heterogeneous oxidation, both on the external surface of the coal particle and internally. Under some conditions a coal particle may burn with very little change in diameter, the particle density decreasing because of internal burning. The rate at which coal particles smaller than about 100 μm burn is, at temperatures below about 2000–2500°K, controlled by chemical kinetic processes. Diffusion of oxygen to the particle surface limits the rate of combustion of larger particles.

On heating, coal swells and becomes hollow or porous [28, 32, 55–59]. The degree of swelling depends on both the coal type and the combustion conditions. Hollow char particles, known as cenospheres, may be formed, particularly if the heating takes place in a reducing atmosphere [55].

Porous vesicular particles are more likely to form if the heating occurs in an oxidizing environment. Coal particles burn on both external and internal surfaces, so as a particle burns, fragile, lacy char structures are formed that eventually disintegrate [28, 56–59].

Ramsden [28] has postulated that mineral inclusions in coal particles melt within the carbon lattice as the combustion front approaches. Water vapor, carbon dioxide, and other gases are evolved because of the temperature rise. If the heating occurs sufficiently rapidly, the sudden increase in pressure within an inclusion and the decrease in the ash viscosity may shatter the inclusion, dispersing the ash into minute droplets. This dispersal may be accompanied by the disintegration of the carbon framework, releasing submicron particles into the gas stream, or the droplets may remain within the carbon framework and coalesce into a liquid layer. The ash has very high surface tension and does not wet the carbon surface. Therefore as the receding carbon surface brings molten inclusions into contact, the ash may coalesce to form spherical droplets larger than the original mineral inclusions. If the temperature of the particle is below the fusion point, the ash inclusions will not coalesce but may agglomerate and, if the temperature is not too low, sinter to form irregularly shaped ash particles. Hollow spherical fly ash particles, known as cenospheres, may form if gas evolution occurs within the particles at temperatures sufficiently high ($T \gtrsim 1200°K$) for the ash to be fluid but low enough ($T \lesssim 1500°K$) that the viscosity prevents the particles from expanding so rapidly that they burst [26, 33, 34]. Cenospheres are usually large ($d_p \gtrsim 50$ μm) and, in large furnaces, account for no more than a few percent of the fly ash mass [26]. Fly ash particles containing bubbles have also been observed [24]. These particles may be formed at temperatures too low to result in cenosphere formation. Cenospheres that contain fly ash or char particles, called plerospheres [34], are probably formed from these particles.

Only a few of these processes need be considered to describe the formation of the dense fly ash particles that account for most of the mass of the particulate matter produced. These processes are summarized in Fig. 4. As a coal particle burns, the mineral inclusions melt and, when the receding carbon surface brings them into contact with one another, coalesce. Because of internal burning, the char particle may break up into a number of fragments. Thus more than one ash particle may be produced from each coal particle, but the total number of ash particles produced may be much less than the total number of mineral inclusions in the coal particle.

Laboratory experiments in which size segregated coal samples were burned in a laminar flow furnace have demonstrated the relationship

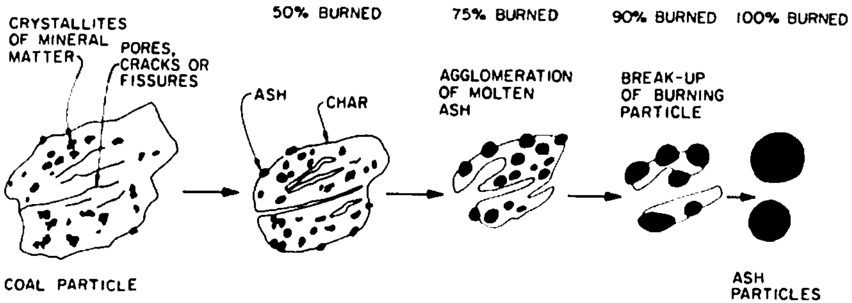
50% BURNED
75% BURNED
90% BURNED
100% BURNED
CRYSTALLITES OF MINERAL MATTER
PORES, CRACKS OR FISSURES
ASH
CHAR
AGGLOMERATION OF MOLTEN ASH
BREAK-UP OF BURNING PARTICLE
COAL PARTICLE
ASH PARTICLES

Fig. 4. Breakup mechanism for the formation of large fly ash particles.

between the coal particle size distribution and the size of large, dense ash particles produced during combustion [33]. Two size cuts, 38–45 μm and 75–90 μm, of two coals, a Pennsylvania bituminous coal and a Montana lignite, were burned under nearly constant temperature conditions. The swelling bituminous coal formed more cenospheres than did the relatively nonswelling lignite. Cenospheres were removed from the ash samples by density segregation in water. The ash particles denser than water were then sized by electron microscopy. Because of the sampling system, which used water to cool the ash, the density segregation system, and the large numbers of particles collected on the electron microscope grids, only particles larger than a few microns in diameter could be counted reliably. The measured size distribution of the ash particles could be correlated with the coal particle size by assuming that three ash particles per lignite particle and about five ash particles per bituminous coal particle were produced during combustion. These numbers are consistent with the expectation that the highly porous char particles formed by the highly swelling bituminous coal would break up into a larger number of fragments than the relatively nonswelling lignite. The number of ash particles produced per coal particle did not vary significantly over a factor of 2 change in the coal particle size.

Application of this breakup model to the formation of large fly ash particles in coal fired combusters requires knowledge of the coal particle size distribution, the ash forming characteristics of the coal being burned, and the combustion conditions. These data are not available for any studies in which the ash particle size distributions were also measured. Most measurements of coal particle size distributions have been made by mechanical sieving of the coal and provide little information about particles smaller than 50 μm. Measurements made using aerodynamic sizing and microscopy provide some data on the quantities of particles as small as a few microns in diameter, but the data are limited. Littlejohn [41] measured the size distribution of pulverized coal as supplied to the burners in a number of boilers. The coal particle size distribution varied considerably from one installation to another. The ash content was also found to vary with coal particle size as a result of the design of pulverizers. The pulverized coal is removed from the mills aerodynamically. Since the mineral density, 2–6 g cm^{-3}, is higher than the coal density, about 1.3 g cm^{-3}, particles that contain significant quantities of mineral matter tend to remain in the pulverizers longer than do particles with a lower mineral content. The finest particles measured by Littlejohn, of about 14 μm diameter, included many consisting entirely of mineral matter and had a mean ash content as much as two times higher than the bulk of the coal.

In spite of these complications, we use these data to test the breakup model for ash formation. For the present purposes we assume that the mineral matter is uniformly distributed through all the coal particles and that p equal mass ash particles are produced from each coal particle. We further assume that the number of ash particles produced is independent of the coal particle size and the density of the ash particles is constant. If the mass fraction of ash in the coal is α (typically 5–20%), a coal particle of mass m produces p particles of mass $m = \alpha m'/p$. Noting that the ash density ρ_a is greater than the coal density ρ_c, the volume of the ash particles produced is

$$v = \frac{\alpha_v v'}{p} \tag{1}$$

where

$$\alpha_v = \alpha\left(\frac{\rho_c}{\rho_a}\right) \tag{2}$$

If the coal particle size distribution is $n_c(d_c)$, the ash particle size distribution is

$$n(d_p) = p\left(\frac{p}{\alpha_v}\right)^{1/3} n_c\left(d_p\left(\frac{p}{\alpha_v}\right)^{1/3}\right) \tag{3}$$

It is unlikely that the burnout of coal particles will result in the formation of ash particles smaller than the original mineral inclusions. For this reason the predicted ash size distribution has been truncated at the particle size where the ash particles predicted by the breakup model are the same size as the mass mean inclusion size. Below this size the coal particles are not expected to contain enough separate mineral grains to produce more than one ash particle per coal particle. These fine ash particles are assumed to have the same size distribution as the mineral inclusions in the coal and to be unaffected by the coal particle size.

These calculations are compared in Fig. 5 with the mass size distribution data of McCain et al. [1], normalized with respect to the total mass of aerosol expected from a coal containing 10% ash burned at a fuel–air equivalence ratio of 0.85, that is, 15% excess air, with no loss of ash to the boiler walls. The data (solid points) are the averages of the measurements obtained at the electrostatic precipitator inlets of six pulverized coal fired power plants. The curve is the prediction of the breakup model assuming that the coal contains 10% ash and that the coal and ash densities are 1.3 and 2.3 g cm^{-3}, respectively, and using a Rosin–Rammler mass distribution, which Field [40] suggests is typical for pulverized coal:

$$dM/d(d_p) = \left(\frac{1.2M}{d_p}\right)\left(\frac{d_p}{53\mu\text{m}}\right)^{1.2}\exp\left(-\left(\frac{d_p}{53\mu\text{m}}\right)^{1.2}\right) \qquad (4)$$

where M is the total mass of coal per unit volume. It is assumed in this calculation that $p=4$. The coal size data of Littlejohn [41] are used to illustrate the sensitivity of the ash particle size distribution to the value of p points. Values of $p=1$ (diamonds), $p=4$ (squares), and $p=10$ (circles) are illustrated. In spite of the large uncertainty in the coal size data and the use of coal size data and breakup model parameters derived in systems different from those in which the measurements were made, the calculations are in qualitative agreement with the data. Part of the discrepancy may be due to the arbitrary parameters used to estimate the total mass loading used in normalizing the fly ash data. The available coal size data permit predictions of ash size distributions only for particles larger than a few microns in diameter.

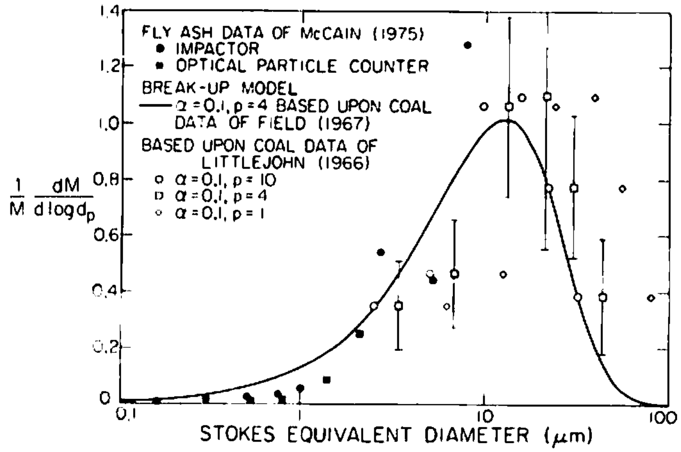

Fig. 5. Comparison of the mass distribution calculated using the breakup model with the fly ash size distribution measured upstream of electrical precipitators on coal fired power plants. The error bars on the $p=4$ points indicate the standard deviation in the calculated size distribution that results from the highly variable coal particle size distribution data of Littlejohn [41].

The fly ash number size distribution provides more information about the submicron particles. McCain et al. [1] have measured the distribution of submicron fly ash particles by using a combination of particle sizing

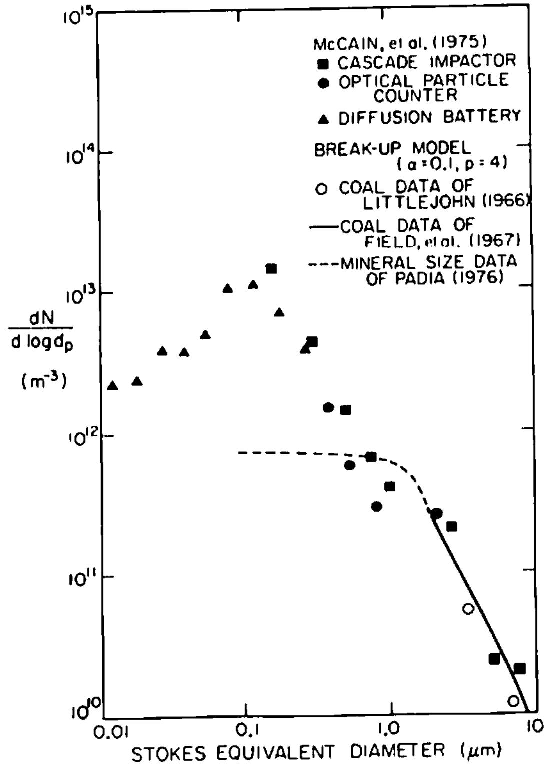

Fig. 6. Comparison of the number distribution predicted using the breakup model with the data of McCain et al. [1].

techniques, including a cascade impactor, an optical particle counter, and a diffusion battery. These data are presented in Fig. 6. The predictions of the breakup model for fly ash particle formation were made assuming $p=4$ and using the assumptions described earlier for ash constant and combustion conditions. The solid line is the prediction made using the coal size distribution of Field [40] and the open points are based on the data of Littlejohn [41]. The broken line shows the effect of truncating the size distribution with mineral size data obtained by Padia [33] for bituminous coal. The total number of particles predicted by this model is much less than the number measured by McCain et al. [1]. It does, however, show very close agreement with the measured numbers of particles larger than about 1 μm diameter. The discrepancy between the theory and the data below 1 μm is sufficiently large that minor changes in the parameters used in the calculations do not account for the difference.

6. FINE PARTICLE FORMATION

The simple breakup model predicts the size distribution of fly ash particles larger than the mineral inclusions. The calculated size distribution is in reasonable agreement with the measured volume distribution of fly ash, but does not agree with the measured number distribution for particles smaller than about 1 μm diameter. A mechanism that can produce several fly ash particles from a single mineral inclusion is required to explain the formation of large numbers of fine particles.

Two mechanisms of fine particle production have been identified. Gas evolution inside molten ash particles forms bubbles that may burst, breaking a single molten ash particle into a number of fine droplets [28]. The size of particles produced by this mechanism is not known, but will certainly depend on the ash composition and temperature, both of which strongly influence the viscosity of the ash [37]. Measurements of the contribution of this mechanism to fine particle formation are required before the breakup model can be extended to include this process. Some ash constituents vaporize in the flame. As the combustion products cool or when the chemical form of the volatilized ash changes (e.g., oxidation of SiO to form the less volatile species, SiO_2), the ash may condense. In spite of the high number densities produced by the breakup mechanism, some of the vapor may condense homogeneously to form very fine particles. Soot particles that are about 0.03–0.1 μm in diameter are formed in this manner [22, 23, 28], and there have been observations of production of a very fine silica aerosol, 0.01–0.15 μm in diameter, during coal combustion [35, 36]. The quantity of ash formed by homogeneous nucleation is not known. Homogeneous nucleation can produce finer particles than would be expected by any mechanical breakup process. With the limited data available the relative importance of the two mechanisms for fine particle formation cannot be evaluated.

The quantity of ash in the submicron size range is only a small fraction, 0.5–4% [1], of the total mass produced during combustion. Condensation of volatilized ash could, based on available data, form this mass of submicron sized particles. Silica accounting for as much as 4% of the ash was vaporized in laminar flow furnace experiments [33]. Another 4% ash loss that was not explained by ash decomposition may be the result of ash vaporization (see Fig. 3). Although these data were not obtained in large pulverized coal combustors, they do suggest that ash vaporization could result in the formation of a quantity of fine fly ash comparable to the measured mass of submicron particles. In the following analysis the contribution of homogeneous nucleation to fine particle production is explored qualitatively by assuming that a small fraction of the ash vaporizes during combustion.

Vaporization of 1% of the ash produces about 0.1 g of condensible material per standard cubic meter. Homogeneous nucleation of this ash would yield a very large number of extremely small particles, probably much smaller than 0.01 μm in diameter. These particles may coagulate with other particles produced by homogeneous nucleation, or they may diffuse to the surfaces of the much larger particles produced by the breakup process. In addition, heterogeneous condensation may occur after homogeneous nucleation. These processes reduce the number of particles produced by condensation and increase their average size.

As long as the particles are much smaller than the mean free path of the gas molecules, the evolution of the aerosol produced by homogeneous nucleation may be described by the theory of self-preserving size distributions for the free molecule regime [60, 61]. Previous applications of this theory have dealt with aerosol evolution in constant density systems. Since the temperature in combustion systems may change over nearly an order of magnitude, the analysis of Lai et al. [60] must be modified to treat variable density flows. For a fluid with uniform composition, the kinetic equation for aerosol evolution is [62]

$$\begin{aligned}\frac{\partial n(v,t)}{\partial t} &+ \nabla \cdot n(v,t)\mathbf{u} \\ &= \frac{1}{2}\int_0^v \beta(\tilde{v}, v-\tilde{v})\, n(\tilde{v},t)\, n(v-\tilde{v},t)\, d\tilde{v} \\ &\quad - \int_0^\infty \beta(v,\tilde{v})\, n(v,t)\, n(\tilde{v},t)\, d\tilde{v} \qquad (5)\end{aligned}$$

where v is the particle volume, $\mathbf{u}$ the gas velocity, and β the collision frequency function. It is convenient to write the aerosol size distribution in terms of unit mass of carrier fluid instead of volume, that is,

$$\tilde{n}(v,t) = \frac{n(v,t)}{\rho} \tag{6}$$

Substituting Eq. 6 into Eq. 5 and using conservation of mass, the result is

$$\begin{aligned} \rho\frac{\partial\tilde{n}(v,t)}{\partial t} &+ \rho\mathbf{u}\cdot\nabla\,\tilde{n}(v,t) \\ &= \frac{\rho^2}{2}\int_0^v \beta(\tilde{v},v-\tilde{v})\tilde{n}(\tilde{v},t)\tilde{n}(v-\tilde{v},t)\,d\tilde{v} \\ &\quad -\rho^2\int_0^\infty \beta(v,\tilde{v})\tilde{n}(v,t)\tilde{n}(\tilde{v},t)\,d\tilde{v} \end{aligned} \tag{7}$$

The left-hand side represents the substantial derivative

$$\rho\frac{d\tilde{n}}{dt} = \rho\frac{\partial\tilde{n}}{\partial t} + \rho\mathbf{u}\cdot\nabla\,\tilde{n}$$

The right-hand side represents the usual coagulation terms written in terms of number per unit mass. The total number and volume of particles may also be calculated on a mass basis, namely,

$$\begin{aligned} \tilde{N}_s &= \int_0^\infty \tilde{n}(v,t)\,dv \\ \tilde{V}_s &= \int_0^\infty v\tilde{n}(v,t)\,dv \end{aligned} \tag{8}$$

Following the analysis of Lai et al. [60], we find that the total number of fine particles decays according to

$$\frac{dN_s}{dt} = -\frac{1}{2}\left[\frac{3}{4\pi}\right]^{1/6}\left(\frac{6kT}{\rho_p}\right)^{1/2}\left(\frac{P}{RT}\right)I_1\tilde{V}_s^{\,1/6}\tilde{N}_s^{\,11/6} \tag{9}$$

where $I_1 = 6.67$ [60] is the dimensionless collision integral. From this result we see that the rate of loss of particles due to coagulation varies inversely with the 1/2 power of the temperature.

The number and size of the fine particles also change by diffusion of fine particles to larger particles and heterogeneous condensation. The self-preserving theory is a reasonable approximation for the evolution of the fine aerosol if the rate of loss of fine particles to the surfaces of larger particles is slow compared to the rate of coagulation and the rate of particle growth by condensation is small compared to the growth by coagulation. The number of particles of size d_s to $d_s + d(d_s)$ diffusing to the surface of a large particle of size d_L per unit time is

$$F = \frac{2\pi D(1+\mathrm{Kn}_L)\tilde{n}_s(d_s)d(d_s)}{(1+1.71\mathrm{Kn}_L+1.333\mathrm{Kn}_L^2)} \tag{10}$$

where $\mathrm{Kn}_L = 2\lambda/d_L$ is the Knudsen number and the Fuchs and Sutugin interpolation formula [63] has been used to describe the diffusion of particles in the transition regime. The total rate of loss of small particles to all large particles is

$$\left(\frac{d\tilde{N}_s}{dt}\right)_D = \frac{-I_DI_2(2\pi mkT)^{1/2}\tilde{N}_s^{5/3}\tilde{V}_s^{-2/3}}{(\frac{2}{3})(1+\pi\alpha_c/8)(6/\pi)^{2/3}} \tag{11}$$

The diffusion integral is defined as

$$I_D = \int_{d_L}\frac{(1+\mathrm{Kn}_L)d_L\tilde{n}_L(d_L)d(d_L)}{(1+1.71\mathrm{Kn}_L+1.333\mathrm{Kn}_L^2)} \tag{12}$$

and is a function of temperature since $\lambda^{a}T$. The integral

$$I_2 = \int_0^\infty \psi(\eta)\eta^{-2/3}\,d\eta \tag{13}$$

has a value of 1.87. Thus total rate of decay of the number of particles is the sum of Eqs. 9 and 11, that is,

$$\begin{aligned} \frac{d\tilde{N}_s}{dt} = &-\left(\frac{I_1}{2}\right)\left[\frac{3}{4\pi}\right]^{1/6}\left(\frac{6kT}{\rho_p}\right)^{1/2}\left(\frac{P}{RT}\right)\tilde{V}_s^{\,1/6}\tilde{N}_s^{\,11/6} \\ &-\frac{I_DI_2(2\pi mkT)^{1/2}\tilde{N}_s^{5/3}\tilde{V}_s^{-2/3}}{\left[\left(\frac{2}{3}\right)(1+\pi\alpha_c/8)(6/\pi)^{2/3}\right]} \end{aligned} \tag{14}$$

It is important to note that this equation is valid only if the magnitude of the second term is much smaller than that of the first term.

The volume of small particles also decreases as a result of diffusion to the surface of large particles. The rate of decay of the volume of fine particles is

$$\frac{d\tilde{V}_s}{dt} = \frac{-I_D I_3\left(\frac{3}{2}\right)(2\pi mkT)^{1/2}(\pi/6)^{2/3}\tilde{N}_s^{2/3}\tilde{V}_s^{1/3}}{(1+\pi\alpha_c/8)} \tag{15}$$

where

$$I_3 = \int_0^\infty \eta^{1/3}\psi(\eta)\,d\eta = 0.885 \tag{16}$$

This model for the evolution of the size distribution has been used to examine the contribution of homogeneous nucleation to the formation of submicron ash particles. Several important assumptions were made. The large particle size distribution given by the breakup model was assumed to be unaffected by coagulation or by diffusion of fine particles to the surfaces of the large particles. This assumption is reasonable for particles larger than 1 μm but may not be appropriate for smaller particles. The furnace, illustrated in Fig. 2, is modeled as a plug flow reactor with uniform composition and temperature at any point. The temperature is assumed to remain constant at a flame temperature of 1800°K for 0.5 sec. The temperature of the combustion products then decreases at a constant rate to the furnace outlet temperature, 1400°K, in 1 sec. Once the combustion products enter the convective heat exchangers, heat transfer is more rapid; the temperature decreases to 425°K in 2 sec. It was further assumed that 1% of the fly ash was vaporized during combustion and immediately condensed by homogeneous nucleation.

The fly ash size distribution calculated using this model is shown in Fig. 7. The total number of particles predicted is an order of magnitude greater than the measured value, and the calculated size distribution has a narrow peak at a particle diameter of about one-fifth that of the broader peak of the measured distribution. Although the predicted small particle number concentration is too large, we estimate that only one-fourth of the fine particle volume is lost by diffusion to the surfaces of the larger particles. We can, therefore, neglect the second term of Eq. 14 in the examination of the causes of this large discrepancy.

The total number of particles is obtained by integrating Eq. 9 with the assumption that the number initially is infinite:

$$\tilde{N}_s = \left(\tfrac{5}{6}K\tilde{V}_s^{1/6}\tau\right)^{-6/5} \tag{17}$$

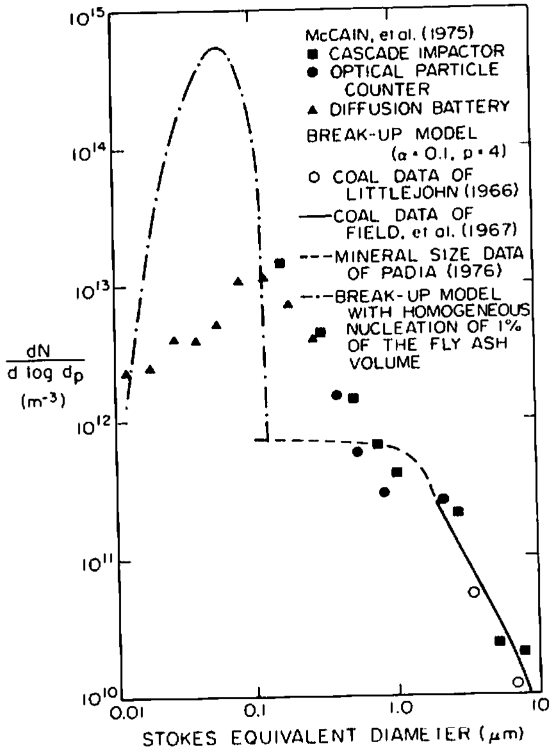

Fig. 7. Comparison of the number distribution calculated using the breakup model with homogeneous nucleation of 1% of the ash with the measured size distribution.

where

$$K = \left(\frac{I_1}{2}\right)\left[\frac{3}{(4\pi)}\right]^{1/6}\left(\frac{6kT_0}{\rho_p}\right)^{1/2}\left(\frac{P}{RT_0}\right)$$

$$\tau = \int_0^t \sqrt{T_0/T}\,dt \tag{18}$$

and T_0 is an arbitrary reference temperature. The total number of particles is proportional to $\tau^{-6/5}$. Even with this strong dependence on the residence time, increase in the residence time alone cannot account for all the discrepancy. The residence time would have to be increased by about a factor of 30 to bring the calculations into reasonable agreement with the measurements. Such a factor would not be reasonable for the usual combustion conditions.

Interparticle dispersion forces increase the rate of coagulation of aerosols in the free molecule regime by a factor that depends on the sizes of the colliding particles and the ratio $A/(kT)$ [61]. The Hamaker constant A depends on the nature of the two interacting materials. Graham and Homer [61] have estimated the effect of dispersion aerosols on the coagulation of a free molecular aerosol of lead with a self-preserving size distribution. The coagulation rate increased by a factor of 2 for a value of $A/(kT)=15$ and a factor of 2.5 for $A/(kT)=39$. The Hamaker constant of silica is $6-12\times 10^{-13}$ erg [64, 65]. The ratio A/kT is in the range 1.7–30 for a silica aerosol in a combustion system. Based on the calculation of Graham and Homer [61], we estimate that the coagulation rate increases by less than a factor of 2.5. Thus dispersion forces may reduce the total number of particles by as much as a factor of 3, but cannot account for the full difference between the measured and calculated number of particles.

The number of ash particles depends only weakly on the volume of ash in the fine particle mode,

$$\tilde{N}_s \propto \tilde{V}_s^{-1/5} \tag{19}$$

however, the size of the particles produced is a somewhat stronger function

$$d_s = \left(\frac{6}{\pi}\cdot\frac{\tilde{V}_s}{\tilde{N}_s}\right)^{1/3} \propto \tilde{V}_s^{2/5} \tag{20}$$

Thus an increase in the concentration of the condensing species would reduce the number and increase the size of the particles produced by homogeneous nucleation. A large change in concentration is required to produce a significant change in the aerosol characteristics.

The composition of the gas in a flame is highly nonuniform. Although a furnace is supplied with excess air, regions of the combustion zone have greater than the stoichiometric fuel–air ratio. Spatial variations in composition occur in the regions of fuel and air injection, and some spatial inhomogeneity may persist throughout the flow. Localized fluctuations in composition that are dissipated by turbulence are also important to aerosol evolution. Corrsin [66] has shown that second order kinetic processes, such as aerosol coagulation, are accelerated by these small scale fluctuations in composition.

Several processes not considered in the model may have major influence on the particle size distribution. Heterogeneous condensation may increase the size of the fine particles. Highly volatile ash constituents may condense after large numbers of particles have been produced by the homogeneous nucleation of less volatile species. Because of the very large surface area of the fine particles, the more volatile compounds may condense on existing particles. Species other than ash may also condense on the fine particles. Sulfur trioxide and water vapor are both present in the combustion products. As the combustion products cool, these two species may react to form sulfuric acid and condense.

Some of the fine particles are soot rather than fly ash. The quantity of soot produced during coal combustion is not known. Soot is formed by the condensation and subsequent pyrolysis of high molecular weight hydrocarbons [22]. These soot precursors are formed only in very fuel-rich regions of flames. The soot particles burn readily in the presence of oxygen at combustion temperatures but burn very slowly at lower temperatures [67]. Relatively minor changes in combustion conditions may result in substantial changes in the quantity of soot produced. In a recent study, combustion modifications designed to reduce emissions of oxides of nitrogen resulted in a factor of 5 increase in the number of particles in the range 0.01–0.1 μm diameter [20], the typical size range for soot particles.

Until the chemical composition of the submicron particles is known, we can only speculate about the relative importance of ash, sulfates, and soot. The contributions of these components may vary significantly from one combustor to another. The formation of fine ash and soot particles is dependent on combustion conditions. Sulfates may be present as either gases or particles, depending on the flue gas temperature at the point where the sample is taken.

Finally, the discrepancy between the model calculations and the measured number of submicron particles may be attributed in part to uncertainties in the experimental measurements. Even diluting the sample by a ratio of 1000 : 1, the number concentration of particles measured is sufficiently high (initially 10^{13} m^{-3} measured and 2×10^{14} m^{-3} calculated) that either the diffusion battery-condensation nuclei counter system [1] or the electrical aerosol analyzer [20] might not be able to count all the particles. Moreover, neither of the two instruments has perfect size resolution, so it is expected that the measured peak in the number distribution would be somewhat broader than the actual distribution.

7. FINE PARTICLE ENRICHMENT BY VOLATILE SPECIES

A number of ash species vaporize during combustion and later condense either homogeneously or heterogeneously. Homogeneous nucleation produces very fine particles containing the volatile ash species. Heterogeneous condensation may also concentrate volatile species in fine particles. The number of molecules of condensing species condensing per unit time on the surface of a particle of size d_p (number per second) in the free molecule regime ($Kn > 1$) is

$$F_i = \alpha_c \pi d_p^2 \left(\frac{kT}{2\pi m_i} \right)^{1/2} (C_i - C_{i,s}) \tag{21}$$

where C_i is the concentration in molecules per unit volume and $C_{i,s}$ is the saturation concentration. The number of molecules condensing on particles of size d_p per unit mass of particles is

$$\frac{F_i}{\left[\rho_p(\pi/6)d_p^3\right]} \propto d_p^{-1} \tag{22}$$

Thus the concentration of a condensing species on particles in the free molecule regime is expected to be inversely proportional to the particle diameter.

In the continuum regime, $\mathrm{Kn} < 1$, the number of particles and the number of molecules condensing per unit time on a particle is

$$F_i = 2\pi d_p D(C_i - C_{i,s}) \tag{23}$$

Thus the number of molecules of the condensed species per unit mass of particles is inversely proportional to the square of the particle diameter, for example,

$$\frac{F_i}{\left[\rho_p(\pi/6)d_p^3\right]} \propto d_p^{-2} \tag{24}$$

Composition–size distribution data are available for a number of fly ash species in particles larger than about 1 μm diameter, that is, the continuum size range even at the highest temperatures in a furnace [11–17]. Davison et al. [11] have shown that the concentrations of several volatile ash constituents were well correlated with the particle size by the expression,

$$\bar{C} = C_0 + \frac{6C_s}{\rho_p d_p} \tag{25}$$

which is consistent with adsorption on the particle surface. The data are also well correlated by Eq. 24 as is shown in Fig. 8. The correlations of the concentrations of the species that exhibited the most pronounced increase in concentration with decreasing particle size are summarized in Table 2. The linear correlation coefficients calculated using both models are comparable for all species considered. These data are not sufficient to differentiate between condensation and adsorption. Sulfur is present in fine fly ash particles in concentrations too large to be explained by adsorption alone, so it appears that some species do condense [11]. The existence of a surface layer containing high concentrations of volatile ash species has recently been confirmed by ion microprobe studies on large fly ash particles [68].

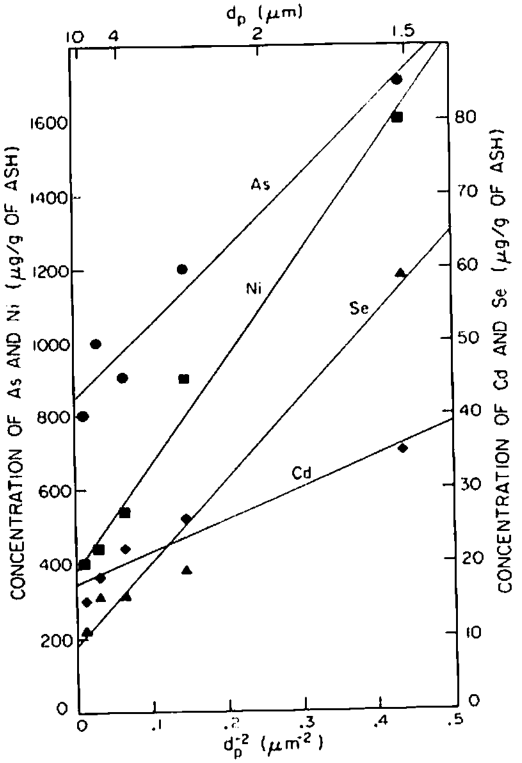

Fig. 8. Dependence of element concentration on particle size fly ash emitted from a coal fired power plant [11].

There are few data on the composition–size distribution for submicron fly ash particles. Ragaini and Ondov [16] observed two peaks in the number distribution, a sharp peak occurring at about 0.1 μm diameter and a second peak at about 1 μm. A number of species were found in the

Table 2. PARAMETERS DERIVED FROM SURFACE DEPOSITION MODELS

	Present Work			Davidson et al. [11]		
	$c = a + b/d_p^2$			$c = C_0 + 6C_i/(\rho_p d_p)$		
Element	a (μgg^{-1})	b ($\mu g \cdot \mu m^2 g^{-1}$)	Linear Correlation Coefficient	C_0 (μgcm^{-2})	C_i (μgg^{-1})	Linear Correlation Coefficient
Pb	1400	530	0.58	0.04	1000	0.73
Tl	55	53	0.71	0.003	40	0.80
Sb	30	54	0.97	0.007	20	0.93
Cd	17	43	0.96	0.002	10	0.99
Se	9	110	0.98	0.004	0.7	0.92
As	850	2000	0.98	0.009	600	0.97
Zn	7400	16000	0.59	0.6	6000	0.60
Ni	770	2900	0.99	0.1	100	0.98
Cr	220	7200	0.99	0.3	300	0.94

smaller peak in much higher concentrations than in the larger peak. The data are only qualitative, however, since neither the total mass loading of the collected aerosol nor the quantities of particles larger than about 3 μm were reported.

The condensation of a volatile species onto the submicron ash can be explored by a simple calculation. The rate of condensation onto particles over the entire range of particle sizes can be described by using the Fuchs and Sutugin interpolation formula [63], for example,

$$F_i = \frac{2d_p D_i(1+K_n)}{(1+1.71K_n+1.333K_n^2)(C_i - C_{i,s})} \tag{26}$$

The total deposition rate (molecules $\sec^{-1}$ g^{-1}) of a species condensing at a temperature T on an aerosol with a size distribution $\bar{n}(d_p, t)$ is

$$f_i(d_p, T) = \int_0^{\infty} F_i(d_p, T)\bar{n}(d_p, t)d(d_p) \tag{27}$$

The calculated condensation rate distribution of a species condensing on particles with the size distribution measured by McCain et al. [1] is shown in Fig. 9.

This result suggests that the majority of a species condensing at this temperature would be concentrated in the submicron particles. If the

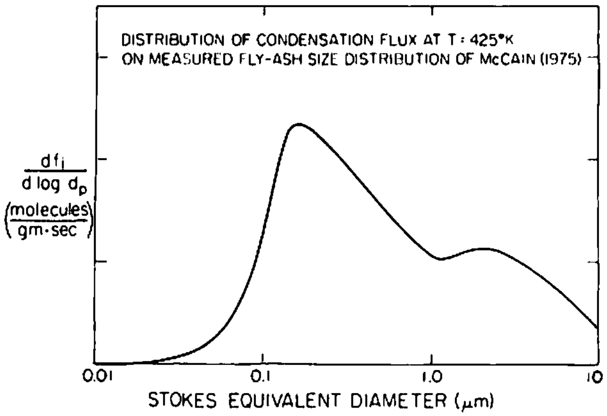

Fig. 9. Calculated distribution of condensation flux to the size distribution measured by McCain et al. [1].

condensation took place earlier in the evolution of the aerosol, the enrichment of submicron particles would be increased because of the larger surface area per unit mass of the smaller particles.

A volatile species that condenses by homogeneous nucleation would probably be uniformly distributed over submicron sized particles since the fine particles undergo considerable growth by coagulation. These fine particles diffuse to the surfaces of larger particles, that is, $F_i \alpha d_p$. Thus we again find that the concentration of the condensing species on particles in the continuum regime would be proportional to d_p^{-2}.

8. SULFATE FORMATION

The particulate matter produced during coal combustion contains high concentrations of sulfur [11]. As has been observed with other volatile species, the sulfur concentration is greater in fine particles than in larger particles. This may be due to the condensation of sulfur trioxide and water to form a sulfuric acid mist. Although only a small fraction of the sulfur in coal is oxidized to form SO_3, the sulfur trioxide has a major impact on boiler operation and aerosol characteristics. Most boiler corrosion appears to be related to the formation of sulfates from SO_3 [37]. The sulfate concentration of fly ash has a strong effect on its electrical resistivity and thus on the collection efficiency of electrical precipitators. The fly ash produced by combustion of low sulfur coals is difficult to remove because of its high electrical resistivity. At some power plants that burn low sulfur coal, SO_3 is added to the flue gases to improve precipitator efficiency.

Cullis and Mulcahy [38] have provided a comprehensive review of the literature on sulfur chemistry and the formation of SO_3 and sulfates in combustion systems, so we only briefly discuss some of the important points influencing the formation of sulfate aerosols within a coal fired boiler. Sulfur contained in fossil fuels is rapidly oxidized to form SO_2 in the high temperature combustion region. Generally less than a few percent of the SO_2 is oxidized to form SO_3 even in the presence of excess oxygen. The thermodynamic equilibrium

$$SO_2 + \tfrac{1}{2}O_2 = SO_3 \tag{28}$$

favors SO_3 formation at ambient temperatures. In the presence of the stoichiometric proportion of oxygen at atmospheric pressure, the equilibrium fractions of the sulfur present as SO_3 rather than SO_2 at 575, 775, and 1275°K are about 1, 0.5, and 0.0, respectively. Increasing the oxygen concentration two orders of magnitude changes these figures to about 1, 0.95, and 0.02.

The primary reaction leading to SO_3 production appears to be

$$SO_2 + O + M \rightleftharpoons SO_3 + M \qquad \Delta h_R = -83 \text{ kcal mole}^{-1} \tag{29}$$

Since the concentration of oxygen atoms is much higher than its equilibrium value within the flame front, SO_3 is formed in much greater than equilibrium concentrations in the flame front [38]. This superequilibrium SO_3 concentration decreases toward the equilibrium value as the combustion products cool.

The equilibrium SO_3 concentration increases with decreasing temperature, but the low equilibrium oxygen atom concentration prevents the formation of SO_3 via the reaction in Eq. 29 at temperatures lower than about 1375°K. Thus the homogeneous gas phase formation of SO_3 occurs primarily in the furnace when temperatures are higher than this value (Fig. 2). Catalysis by heat transfer surfaces of particles may facilitate SO_3 formation at lower temperatures in the convective passes of the boiler.

The total SO_3 formed by homogeneous chemistry in a flame generally accounts for about 1% of the sulfur. Under normal combustion conditions, 10–30% excess air, the conversion of SO_2 to SO_3 is insensitive to the amount of oxygen present in the combustion products as is shown in Fig. 10 [69]. The SO_3 concentration decreases rapidly, however, as the quantity of excess air is reduced.

Catalytic oxidation of SO_2 may occur on the surfaces of fly ash particles in boilers. Ferric oxide and vanadium pentoxide are both efficient catalysts for SO_3 formation. Other species present in the fly ash may reduce the effectiveness of these materials as catalysts. The relative importance of homogeneous chemistry and catalysis to the formation of SO_3 has been a source of controversy. The strong dependence of the SO_3 concentration on the oxygen concentration in the range 0–3% O_2 and the much weaker dependence at high oxygen concentrations is the strongest evidence that most of the SO_3 is formed in the flame. A catalytic mechanism would be expected to produce more SO_3 with increasing oxygen concentration beyond the 3% level. Moreover, the levels of SO_3 produced in coal fired boilers are comparable to those produced in the absence of catalysts.

Sulfur dioxide may also react with ash constituents and metal surfaces. Sodium accounts for about 0.02–0.15% of the coal mass; potassium is about 0.08–0.3% of the coal [47]. These two species readily form sulfates, which are the source of many of the corrosion problems in coal fired boilers. Sodium salts are completely converted to atomic sodium in the high temperature regions of a flame. Sodium intermediates may react with SO_2 or SO_3 to form Na_2SO_4 in the flame, or it may be formed on surfaces. Sodium sulfite is formed under reducing conditions. The chemistry of

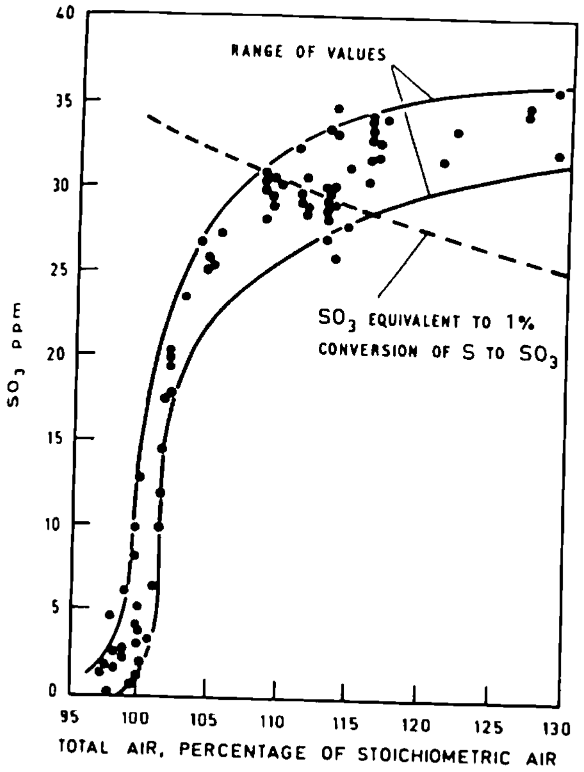

Fig. 10. Effect of excess air on the formation of SO_3 in premixed combustion of natural gas with 5.5 weight percent S as H_2S. (After Ref. 68.)

formation of alkali sulfates and sulfites in flames is poorly understood. Sulfur oxides may also react with other metal oxides, such as Fe_3O_4 [70], to form sulfates.

Sulfur trioxide in the flue gases increases the dew point to as high as 430°K. When the combustion products are cooled below this temperature, SO_3 may condense with water to form sulfuric acid droplets. This condensation may account for a significant fraction of the fine particle mass and cause severe corrosion when it occurs in the boiler or stack. Stack temperatures are usually maintained at higher levels than the dew point to prevent condensation within the plant.

9. CONCLUDING COMMENT

This chapter has reviewed the current understanding of the processes involved in particle formation during the combustion of pulverized coal. Ash derived from the mineral matter in coal accounts for the major portion of the particulate matter produced. It is also the source of many potentially toxic constituents of the particulate emissions. A number of processes that contribute to fly ash formation are summarized in Fig. 11. We have seen that the particle size distribution of ash particles larger than about 1 μm diameter can be related to the coal particle size distribution. This model was based on observations of ash particle formation under conditions similar to those occurring in conventional pulverized coal combustion. New combustion systems may have much different emission characteristics. If coal is burned at temperatures below the ash fusion temperature, the mineral inclusions in a burning coal particle may not agglomerate. The size of the ash particles produced in such a system (e.g., a fluidized bed combustor) may more closely resemble the size distribution of the mineral grains than the coal size distribution. Very high temperature combustion, such as in magnetohydrodynamic power generation, would certainly increase the quantity of ash vaporized.

The formation of submicron sized particles probably occurs by homogeneous nucleation of volatilized ash, soot, and sulfates as well as by the breakup of burning coal particles. The relative contributions of these components can only be determined by further experimental work. Chemical analysis of the submicron aerosol can provide valuable information on the sources of fine particles.

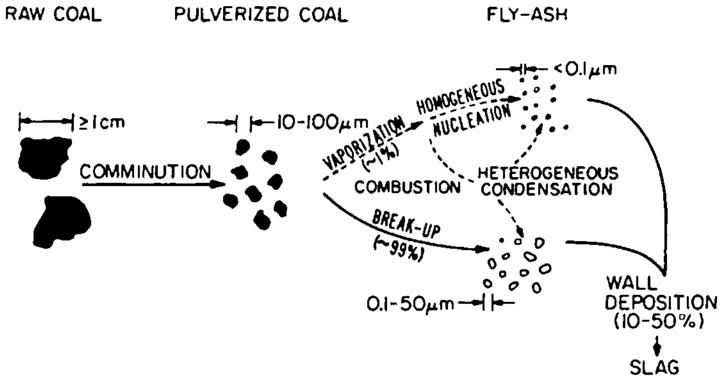

Fig. 11. Processes that contribute to fly ash particle formation.

Simple calculations have shown that condensation can result in substantial enrichment of submicron particles with volatile species. The fraction of a vapor that condenses on fine particles is a strong function of the particle size distribution. The calculations were for heterogeneous condensation on the aerosol present at the inlet to the electrostatic precipitator on a coal fired power plant. This aerosol may contain sulfuric acid and water, which condense at low temperatures. If these components contribute significantly to the submicron aerosol, the surface area of submicron particles available for condensation at higher temperatures is smaller than was assumed in our calculations. The quantity of an ash component that condenses on submicron particles may therefore be less than our calculations suggest. The quantities of sulfuric acid and water contained in the fine particles is not known. Measurements of the composition-size distribution of the fine particles present upstream of gas cleaning equipment will be required to determine the degree to which fine particles are enriched with volatile species.

ACKNOWLEDGMENT

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REFERENCES

1. J. D. McCain, J. P. Gooch, and W. B. Smith, *J. Air Poll. Control Assoc.*, **25**, 117–121 (1975).
2. O. I. Joensuu, *Science*, **172**, 1027–1028 (1971).
3. K. K. Bertine and E. D. Goldberg, *Science*, **173**, 233–235 (1971).
4. C. E. Billings and W. R. Matson, *Science*, **174**, 1232–1233 (1972).
5. D. H. Klein and P. Russell, *Environ. Sci. Technol.*, **7**, 357–358 (1973).
6. A. W. Andren, D. H. Klein, and Y. Talmi, *Environ. Sci. Technol.*, **9**, 856–858 (1975).
7. C. Block and R. Dams, *Environ. Sci. Technol.*, **9**, 146–150 (1975).
8. C. Block and R. Dams, *Water, Air, Soil Pollut.*, **5**, 207–211 (1975).
9. D. F. Gatz, *Atmos. Environ.*, **9**, 1–16 (1975).
10. G. E. Gordon, D. D. Davis, G. W. Israel, H. E. Landsberg, T. C. O'Haree, S. W. Staley, and W. H. Zoller, "Atmospheric Impact of Major Sources and Consumers of Energy," Progree Report-75, 1 October 1974 to 31 August 1975, University of Maryland, College Park.
11. R. L. Davison, D. F. S. Natusch, J. R. Wallace, and C. A. Evans, Jr., *Environ. Sci. Technol.*, **8**, 1107–1113 (1974).

12. R. E. Lee, Jr., and D. J. von Lehmden, *J. Air Pollut. Control Assoc.*, **23**, 853–857 (1973).
13. R. E. Lee, Jr., H. L. Crist, A. E. Riley, and K. E. MacLeod, *Environ. Sci. Technol.*, **9**, 643–647 (1975).
14. J. W. Kaakinen, R. M. Jorden, M. H. Lawasani, and R. E. West, *Environ. Sci. Technol.*, **9**, 862–869 (1975).
15. D. H. Klein, A. W. Andren, J. A. Carter, J. F. Emergy, C. Feldman, W. Fulkerson, W. S. Lyon, J. C. Ogle, Y. Talmi, R. I. Van Hook, and M. Bolton, *Environ. Sci. Technol.*, **9**, 973–979 (1975).
16. R. C. Ragaini and J. M. Ondow, "Trace Contaminants from Coal-Fired Power Plants," presented at the International Conference on Environmental Sensing and Assessment, Las Vegas, September 1975.
17. C. Block and R. Davis, *Environ. Sci. Technol.*, **10**, 1011–1017 (1976).
18. L. J. Shannon, P. G. Gorman, and M. Reichel, "Particulate Pollutant Emission Study: Vol. II. Fine Particle Emissions," EPA Report No. APTD 0744, August 1971.
19. E. J. Schulz, R. B. Engdahl, and T. T. Frankenberg, *Atmos. Environ.*, **9**, 111–119 (1975).
20. E. W. Schmidt, J. A. Gieseke, and J. M. Allen, "Size Distribution of Fine Particulate Emissions from a Coal-Fired Power Plant," *Atmos. Environ.*, **10**, 1065–1069 (1976).
21. *Steam, Its Generation and Use*, Babcock and Wilcox, New York, 1972.
22. J. Lahaye, G. Prado, and J. B. Donnet, *Carbon*, **12**, 27–35 (1974).
23. G. P. Prado, M. L. Lee, R. A. Hites, P. P. Hoalt, and J. B. Howard, "Soot and Hydrocarbon Formation in a Turbulent Diffusion Flame," 649–661, The Combustion Institute, 1976.
24. J. D. Watt and D. J. Thorne, *J. Appl. Chem.*, **15**, 585–594 (1965).
25. E. Raask, *J. Eng. Power*, **88**, 40–44 (1966).
26. E. Raask, *J. Institute Fuel*, **41**, 339–344 (1968).
27. A. R. Ramsden, *J. Institute Fuel*, **41**, 451–454 (1968).
28. A. R. Ramsden, *Fuel* (Lond.), **48**, 121–237 (1969).
29. E. Raask, *Fuel* (Lond.), **48**, 366–374 (1969).
30. I. Fells and D. Richardson, *J. Institute Fuel*, **42**, 245–248 (1969).
31. C. A. J. Paulson and A. R. Ramsden, *Atmos. Environ.*, **4**, 175–185 (1970).
32. J. Yerushalani, M. Kolodney, R. A. Graff, and A. M. Squares, *Science*, **187**, 646–648 (1975).
33. A. S. Padia, "The Behavior of Ash in Pulverized Coal under Simulated Combustion Conditions," D.Sc. thesis, Massachusetts Institute of Technology, Cambridge, Mass., January 1976.
34. G. L. Fisher, D. P. Y. Chang, and M. Brummer, *Science*, **192**, 553–555 (1976).
35. P. Murphy, Jr., J. D. Piper, and C. R. Schmansky, *Trans. ASME*, **73**, 821–843 (1957).

36. E. Raask and D. M. Wilkins, *J. Institute Fuel*, **38**, 255–261 (1965).
37. W. T. Reid, *External Corrosion and Deposits: Boilers and Gas Turbines*, American Elsevier, New York, 1971.
38. C. F. Cullis and M. F. R. Mulcahy, *Combust. Flame*, **18**, 225–292 (1972).
39. B. P. Breen, "Combustion in Large Boilers: Design and Operating Effects on Efficiency and Emissions," presented at the Sixteenth Symposium (International) on Combustion, Cambridge, Mass., August 1976.
40. M. A. Field, D. W. Gill, B. B. Morgan, and P. G. W. Hanksley, *Combustion of Pulverized Coal*, British Coal Utilization Research Association, Leatherhead, England, 1967.
41. R. F. Littlejohn, *J. Institute Fuel*, **38**, 59–67 (1965).
42. R. C. Flagan and J. P. Appleton, *Combust. Flame*, **23**, 249–267 (1974).
43. D. Pratt, *Prog. Energy Combust. Sci.*, **1**, 73–86 (1976).
44. L. Lamb, *J. Institute Fuel* (Lond.), **45**, 443–448 (1972).
45. S. T. Cuffe and R. W. Gerstle, "Emissions from Coal-Fired Power Plants, A Comprehensive Summary," U.S. Public Health Service Report No. AP-35, 1967.
46. J. V. O'Gorman and P. L. Walker, Jr., *Fuel* (Lond.), **51**, 135–151 (1971).
47. R. R. Ruch, H. J. Gluskoter, and N. F. Shimp, "Occurrence and Distribution of Potentially Volatile Trace Elements in Coal," EPA Report No. EPA-650/2-74-054, July 1974.
48. R. J. Mitchell and H. J. Gluskoter, *Fuel* (Lond.), **55**, 90–96 (1976).
49. C. A. Zappfe, *J.Am. Ceram. Soc.*, **27**, 293–298 (1944).
50. L. Brewer, *Chem. Rev.*, **52**, 1–75 (1953).
51. H. L. Schick, *Chem. Rev.*, **60**, 331–362 (1960).
52. R. J. Ackerman and R. J. Thorn, *Prog. Ceram. Sci.*, **1**, 39–88 (1961).
53. H. Beecher and R. E. Rosenweig, *Amer. Rocket Soc. J.*, **31**, 532–539 (1961).
54. M. Ladadacki, *AIAA J.* **4**, 1445–1447 (1966).
55. F. S. Sinnat, *J. Soc. Chem. Ind.*, Lond. **47**, 151–155 (1928).
56. P. J. Street, R. P. Weight, and P. Lightman, *Fuel* (Lond.) **48**, 343–365 (1969).
57. M. A. Field, *Combust. Flame*, **13**, 237–252 (1969).
58. M. D. Gray, G. M. Kimber, and D. E. Granger, *Fuel* (Lond.) **46**, 399–400 (1967).
59. A. R. Ramsden and I. W. Smith, *Fuel* (Lond.) **47**, 253–256 (1968).
60. F. S. Lai, S. K. Friedlander, J. Pich, and G. M. Hidy, *J. Colloid Interface Sci.*, 39, 395–405 (1972).
61. S. C. Graham and J. B. Homer, *Faraday Symp. Chem. Soc.*, 7, 85–96 (1973).
62. S. K. Friedlander, *Smoke, Dust and Haze: Fundamentals of Aerosol Behavior*, Wiley-Interscience, New York, 1977.
63. N. A. Fuchs and A. G. Sutugin, in *Topics in Current Aerosol Research*, G. M. Hidy and J. R. Brock, Eds., Pergamon, New York, 1971.

64. J. Gregory, *Adv. Colloid Interface Sci.*, **2**, 396–417 (1969).
65. J. Visser, *Adv. Colloid Interface Sci.*, **3**, 331–363 (1972).
66. S. Corrsin, *Phys. Fluids*, **1**, 42–47 (1958).
67. C. Park and J. P. Appleton, *Combust. Flame*, **20**, 369–379 (1973).
68. R. W. Linton, A. Loh, D. F. S. Natusch, C. A. Evans, Jr., and P. Williams, *Science*, **191**, 852–854 (1976).
69. R. E. Barrett, J. D. Hummell, and W. T. Reid, *Trans ASME, J. Eng. Power*, **88**, 165–172 (1966).
70. H. H. Krause, A. Levy, and W. T. Reid, *Trans. ASME, J. Eng. Power*, **91**, 216–222 (1969).

Coal Combustion Aerosol Formation Mechanisms: A Review

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The composition and size distribution of particles emitted by coal combustion sources depend upon various mechanisms leading to their formation. A review of current ideas about possible mechanisms for formation of combustion aerosols is presented. Available data regarding fly ash size distribution and elemental concentrations in various size fractions were analyzed. These data were qualitatively compared with theoretical model predictions to indicate the relative contributions of various mechanisms in the formation of aerosols.

INTRODUCTION

With the anticipated increase in use of coal for electric power generation, there is continued concern about the atmospheric emissions associated with coal. Coal combustion is a major source of particulate emissions into the atmosphere. Emission of fine particles in size range 0.1–5 μm in diameter have relatively long atmospheric residence times and may affect health and visibility. These particles are the most difficult to collect by conventional collection equipment (Burchard, 1974; Shannon, 1974).

There is evidence of enrichment or preferential concentration of certain toxic trace elements (e.g., As, Se, Sb, Zn) in the finer fractions of combustion aerosols (Davison et al., 1974; Kaakinen et al., 1975; Ondov et al., 1979a, b; Smith et al., 1979a, b). This raises the question of the respirable emissions from coal combustion as a potential health hazard. The concentration of these trace species increases with decreasing particle size. Thus, it is important to characterize these emissions to assess adequately their health hazards and to facilitate their control.

Combustion aerosols may be characterized by their size as well as their elemental composition. Their characteristics depend on a number of factors, such as the type and properties of the parent coal and the size distribution of the parent coal particles being burned. The composition–size distributions of particles emitted by coal combustion sources are also influenced by furnace design and operating conditions such as temperature. The combustion aerosols contain primarily inorganic matter associated with coal but may also contain unburnt carbon particles—soot, condensed aromatic hydrocarbons, and sulfuric acid droplets. The size and composition of these aerosols depend upon the mechanisms leading to their formation.

Limited data are available regarding detailed size distribution and chemical composition of coal combustion emissions. Careful analysis of these data is necessary to understand the underlying mechanisms involved in their formation. An extensive review of particle formation in coal combustion was made by Flagan and Friedlander (1978). It is the purpose of this paper to analyze and qualitatively compare the data published since this review.

A brief account of coal properties and overall combustion processes is presented first, followed

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by a survey of proposed particle formation mechanisms. Available data are considered first from a particle size distribution point of view. Elemental size distributions are reviewed next. Qualitative comparison of the data is then made with the predictions from various mechanisms.

PROPERTIES OF COAL

Coal structure and composition have definite influence on resulting emissions. The properties vary greatly with coal origin. Even two samples of coal from the same mine may be significantly different.

Distribution and Variability

Coal is distributed widely throughout the United States in the Appalachian, Illinois, and Western basins. Its chemical and physical properties vary greatly from one region to another, as shown in Table 1. The Eastern coals (Appalachian and Illinois) are generally higher in sulfur and iron, producing a more acidic ash than Western coal. Western coal is generally rich in the lighter elements and low in sulfur with a more alkaline ash. Since an extensive study of coal composition has been compiled by Gluskoter et al. (1977), only a limited review will be presented here.

Coal can also be classified by age, as shown in Table 2. Generally, most of the coal consumed for power generation is either bituminous or subbituminous.

Coal Structure

Coal is a complex, heterogeneous, and variable material. Incorporated within the fossilized carbonaceous material are minerals from the original plant tissue and silt deposited during the formation of the coal. In addition, when the coal seam is mined, overburden may be mixed with the coal. Finkelman (1970), in a microscopic analysis of coal, reported that the minerals are dispersed in the coal with diameters ranging down to the submicron region. Sarofim et al. (1977) reported that the inorganic minerals are widely distributed in size with a mean diameter of 1 μm. In addition, clays composed of sub-

TABLE 1. Selected Coal Analysis for the Major Basins in the United States

	Western (28 samples)		Illinois (144 samples)		Appalachian (23 samples)	
	Arithmetic mean	Min:max	Arithmetic mean	Min:max	Arithmetic mean	Min:max
aluminum (%)	1.0	0.3 : 2.2	1.2	0.42: 3.0	1.7	1.1 : 3.1
calcium (%)	1.7	0.44: 3.8	0.67	0.01: 2.7	0.47	0.09: 2.6
chlorine (%)	0.03	0.01: 0.13	0.14	0.01: 0.54	0.17	0.01: 0.80
iron (%)	0.53	0.03: 1.2	2.0	0.45: 4.1	1.5	0.50: 2.6
potassium (%)	0.05	0.01: 0.32	0.17	0.04: 0.56	0.25	0.06: 0.06
magnesium (%)	0.14	0.03: 0.39	0.05	0.01: 0.17	0.06	0.02: 0.15
sodium (%)	0.14	0.01: 1.60	0.05	— : 0.2	0.04	0.01: 0.08
silicon (%)	1.7	0.38: 4.7	2.4	0.58: 4.7	2.8	1.0 : 6.3
titanium (%)	0.05	0.02: 0.13	0.06	0.02: 0.15	0.09	0.05: 0.15
moisture (%)	18	4.1 :13.7	9.4	0.5 :18	2.7	1.0 : 6.8
volatiles (%)	44	33 :53	40	27 :46	33	17 :42
fixed carbon (%)	46	35 :55	49	41 :61	55	45 :72
ash (%)	9.6	4.1 :20	11	4.6 :20	12	6.1 :25
sulfur (%)	0.76	0.34: 1.9	3.6	0.56: 6.4	2.3	0.55: 5.0
heat value (Btu/lb)	11,409	10,084:12,901	12,712	11,562:14,362	13,111	11,374:13,816

From Gluskoter et al. (1977).

TABLE 2. Composition as a Function of Coal Type

Component	Anthracite	Bituminous	Subbituminous	Lignite
moisture (%)	1.4	4.8	18.4	41.5
vol. matter (%)	6.5	32.3	33.8	23.0
fixed carbon (%)	79.5	51.2	39.0	20.9
ash (%)	12.5	11.7	8.8	14.6
hydrogen (%)	2.4	5.0	5.9	6.8
carbon (%)	80.1	69.1	54.3	29.9
nitrogen (%)	0.8	1.3	1.0	0.5
oxygen (%)	3.2	10.3	29.3	46.5
sulfur (%)	0.8	2.7	0.7	1.7
heat value (Btu/lb)	12,780	12,260	9140	5000
sulfate sulfur (%)	0.02	0.16	0.04	0.24
pyritic sulfur (%)	0.35	1.70	0.35	0.68
organic sulfur (%)	0.48	0.88	0.32	0.75

From Swanson et al. (1976).

micron particles may be incorporated in the coal. It appears from the rather limited studies on coal that the mineral inclusions are submicron and vary over a wide range of sizes. However, very few quantitative data on coal-mineral size distribution exist. Major forms of the minerals appear to be aluminosilicates with pyrites, calcites, and magnesites in various proportions (Gluskoter et al., 1981).

COMBUSTION PROCESS

Qualitative Description

Pulverized firing systems are most commonly used for large modern power plants using coal (Babcock and Wilcox, 1978). The crushed coal from the mine is pulverized into a fine powder, usually 100–200 mesh. The mean mass diameter of coal particles may vary from plant to plant, and the size distribution is usually very broad. The pulverized coal is blown into the furnace with carrier air. Coal particles are heated by radiation and mixing with hot gases. Combustion temperature depends upon percent excess air, quality of coal, and effectiveness of mixing. Temperatures up to 2000°C are usual. Different coal particles may be subjected to varying temperatures due to differences in size and nonuniformity in mixing.

A number of processes may occur during coal-particle burnout. As a coal particle is being heated, it may mechanically break up into fragments because of thermal stresses induced by internal fissures, cracks, and structural imperfections initially present (Flagan and Friedlander, 1978). Volatile fractions originally present in the coal or formed by pyrolysis are vaporized. Chemical decomposition may take place evolving gaseous CO_2, SO_2, and SO_3. A particle may burst open from pressure generated internally by evolution of such gases (Smith et al., 1979b). A heated coal particle swells and may become porous. The degree of swelling depends both on the coal type and combustion conditions.

The general range of behavior of solid particles during gas–solid reactions was discussed by Levenspiel (1962). In extreme cases a coal particle may either retain the ash layer as burning proceeds inward or continuously shed the ash layer as the particle burns and thus shrink in size (Figure 1). The physical state of the ash layer would depend upon ash temperature and mineral composition. The shedding of ash layer may be caused by the evolution of off gases or by cracking or breakup of the particle.

Three temperature ranges that have varying influence on the behavior of mineral inclusions may be indicated. At low enough temperatures the mineral ash inclusions may remain solid. These inclusions may undergo chemical trans-

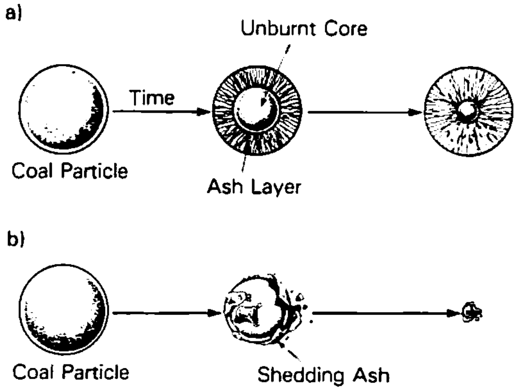


FIGURE 1. Two extreme types of coal particle combustion: coal particle burning (**a**) at constant size and (**b**) with shrinking size.

formations such as decomposition as well as physical transformations such as sintering. A medium temperature range may be designated as the one at which mineral inclusions may fuse, thereby producing highly viscous molten ash. At higher temperatures the viscosity of molten ash is considerably reduced with increased fluidity. The actual temperature values for these ranges would depend upon the mineral ash compositions involved.

The individual mineral inclusions, whether solid or liquid, eventually form the resulting fly ash particles. These inclusions may undergo several physical transformations modifying their size distribution.

Coalescence of Individual Mineral Inclusions. Molten mineral ash inclusions present on a burning coal particle may coalesce and form larger ash droplets. For low combustion temperatures, where the ash remains solid, obviously there would be no coalescences, although some sintering may take place joining adjacent solid small particles. The higher the temperature, the greater the extent of coalescence that may be expected, because of the higher mobility of molten ash. The extent of coalescence may be expected to be greatly reduced with significant shedding of ash. Uncoalesced mineral inclusions and shedded ash may eventually form fine particles.

Bubble Formation. Molten mineral inclusions may come together to form a liquid layer. Gases may evolve within this layer so as to form bubbles. At medium temperatures, because of high viscosity these bubbles may remain stable and form large hollow spheres or cenospheres (Sarofim et al., 1977). At high temperatures, however, these bubbles may burst open owing to lower ash viscosity releasing fine molten ash droplets (Smith et al., 1979b). Bubble-bursting phenomena are not yet well understood, and any conclusive evidence in support of this mechanism has not yet been provided. Based upon aqueous bubble-bursting studies reported in the literature (Tomaides and Whitby, 1975), a broad bimodal droplet size distribution may be expected from such ash bubble bursting. Again in this case, shedding of ash may be expected to reduce the extent of bubble formation.

Evaporation and Condensation of Relatively Volatile Species. An ash species may vaporize depending upon the ash temperature, composition, and relative volatility of the species concerned. The volatility of an element depends on its chemical form in the ash. Thus observed elemental volatilities may be expected to be different from pure element-relative volatilities. Because of the reactive atmosphere near a particle surface, several chemical reactions are possible modifying the volatility of a species. A reducing or oxidizing atmosphere may prevail in the vicinity of a coal particle, depending on the mixing of gases, percent excess air, kinetics of combustion reactions, and presence of an ash layer surrounding the "burning front" that may introduce diffusional effects. Close to a particle surface reducing conditions may be expected whereas slightly away from the coal particle oxidizing conditions may be present in the gas phase. This model was proposed by Levenspiel (1962) to explain solid gas reaction kinetics and is diagramed in Figure 2. The reducing conditions near the particle surface may produce more volatile, reduced species that would vaporize, oxidize in the bulk gas phase away from the particle surface, and subsequently condense owing to the lower volatilities of oxidized species, e.g., SiO (Sarofim et al., 1977).

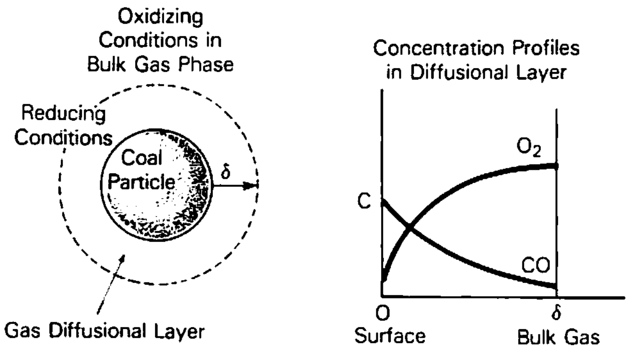

Oxidizing Conditions in Bulk Gas Phase
Reducing Conditions
Coal Particle
δ
Gas Diffusional Layer
Concentration Profiles in Diffusional Layer
C
O_2
CO
O
Surface
δ
Bulk Gas

FIGURE 2. Reducing boundary layer at the particle surface.

The vaporized species may condense downstream upon gas cooling, either homogeneously forming new very fine, rapidly coagulating particles or heterogeneously condensing on existing particles. The fine particles and particle surfaces in general would then be preferentially enriched with volatile species. The degree of enrichment would depend upon the volatility of the species in question.

Homogeneous condensation would result in bulk enrichment of volatilized species in the fine size fractions. Heterogeneous condensation, on the other hand, would result in surface enrichment of the volatilized species. The enrichment would be most prominent in the finer size fractions because of their greater available surface area for condensation per unit volume.

In addition to these three major processes, several other mechanisms are also possible. Some fine mineral inclusions may remain separate without coalescing with others owing to surface tension effects or simply adequate spatial separation from other molten inclusions. These fine inclusions may eventually detach to form fine particles. Extraneous clay particles that adhere to the coal during mining and processing may easily disintegrate, separate out, and pass through the combustion process unchanged. Some fraction of carbon may remain unburnt and appear in the aerosols. Aromatic hydrocarbons may vaporize and burn and partially release fine carbon particles, or soot (Green and Lane, 1964).

The minerals may form solid solutions and may exhibit different properties as compared to individual species in the solution. This apparently affects relative volatilities of some species. Thus, elements structurally incorporated into aluminosilicate matrix tend to show reduced volatility, e.g., Na. A physical rearrangement within the solid solutions similar to dissolution and precipitation may also be possible in varying temperature conditions.

Figure 3 presents a qualitative picture of what might be happening during the combustion and shows the multitude of processes that may be occurring simultaneously.

Particle Formation Mechanisms

Although a number of mechanisms of qualitative nature have been proposed, a semiempirical quantitative treatment has been developed for two mechanisms.

Breakup Model. A detailed account of this model is presented by Flagan and Friedlander (1978). The model considers melting of mineral inclusions followed by coalescence as the combustion front recedes. Each coal particle is then assumed to yield a number P of particles of equal size. Knowing the coal particle size distribution, the mass fraction of mineral ash, and the densities of coal and ash fractions, an ash particle size distribution may be predicted for a given value of P.

The mean mass diameter of ash may be given as adapted from Flagan and Friedlander (1978).

$$\bar{D}_{ash} = \sqrt[3]{\frac{f}{P}\,\frac{\rho_c}{\rho_a}}\;\bar{D}_{coal}. \tag{1}$$

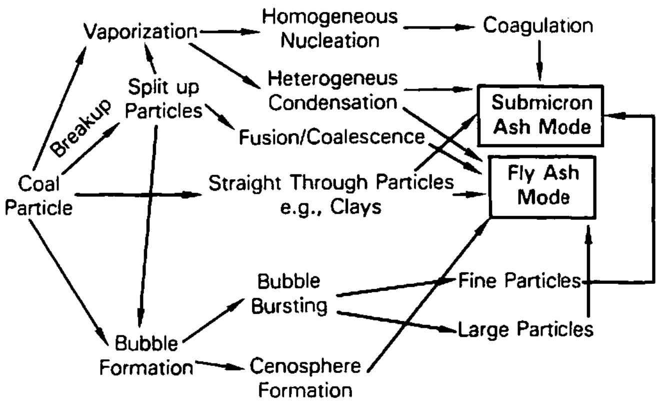

Vaporization
Homogeneous Nucleation
Coagulation
Split up Particles
Heterogeneus Condensation
Submicron Ash Mode
Breakup
Fusion/Coalescence
Fly Ash Mode
Coal Particle
Straight Through Particles e.g., Clays
Bubble Bursting
Fine Particles
Large Particles
Bubble Formation
Cenosphere Formation

FIGURE 3. Schematic of coal combustion aerosol formation.

where

$\bar{D}_{coal}$	is the mass mean diameter of coal (μm),
$\bar{D}_{ash}$	the mass mean diameter of ash (μm),
ρ_c	the density of coal (g/cm^3),
ρ_a	the density of ash (g/cm^3),
P	the number of coal fragments produced per particle, and
f	the mass fraction of ash in coal.

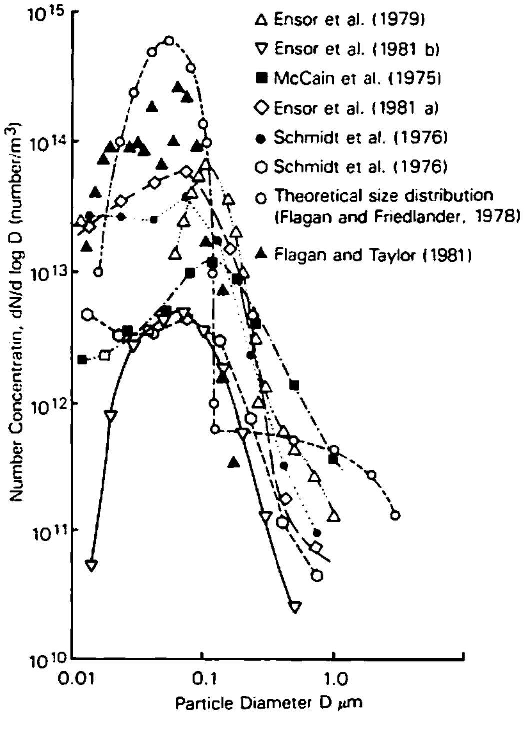
Equation (1) is a simplified view of the ash formation process. The value of P is usually considered to be between 3 and 5. Laboratory studies by Sarofim et al. (1977) are consistent with this model.

Since Eq. (1) implies that the ash forming process from each coal particle is similar in the breakup model, all resulting ash particles are predicted to be similar in their physical, morphological, and chemical nature. No explanation of cenospheres or fine submicron particles is contained in this model.

Vaporization–Condensation Model. This model suggests a mechanism for submicron particle formation. Basically a fraction of ash (~ 1%) is assumed to be vaporized and homogeneously condensed to form primary particles of the order of 10 Å in size, followed by coagulation to yield self-preserving particle-size distribution within a few seconds (Flagan and Friedlander, 1978). Such a process predicts a submicron mode in particle size distribution around 0.1 μm.

The resulting size distribution, when compared with the fine particle data of McCain et al. (1975), was found to predict an order of magnitude larger number of particles with a smaller mean diameter (Figure 4). Flagan (1979) later included accelerated coagulation due to interparticle dispersion and nonhomogeneous

FIGURE 4. Aerosol size distribution in the submicron range.



mixing, which reduced the discrepancy but still predicted larger than observed fine particle densities. Additional recent data (Ensor et al., 1979, 1981a) also showed similar discrepancies between theory and experimental observations.

The model has some flexibility through the empirical parameter — the fraction of ash vaporized. This fraction would actually depend upon ash mineral composition and temperature. The model predicts a sharp submicron mode in mass or number size distribution at about 0.1 μm. Vaporization of species depends upon their relative volatilities. Hence, such a submicron ash mode formed by vaporized material may be expected to be composed primarily of volatile materials, and its composition may be expected to differ significantly from larger particles formed in breakup. This model has also been strongly supported by laboratory combustion studies (Sarofim et al., 1977; Mims et al., 1979; Flagan and Taylor, 1980; Neville et al., 1980).

Other mechanisms that have not been quantified but have been justified by experimental observations are as follows:

1. Bubble formation due to evolution of gases in the coal particles. This mechanism has been supported by the presence of large cenospheres observed microscopically by various investigators. Laboratory studies by Sarofim et al. (1977) indicated the mass fraction of cenospheres to be dependent upon temperature and to peak at 6% at 1500 K.
2. Condensation of volatile species on existing particles to produce surface layers enriched in volatile species. Numerous observations have indicated surface enrichments of volatile species, especially on fine particles. The concentration of certain volatile species has been observed to increase with decreasing particle size. Biermann and Ondov (1980) have recently analyzed their surface enrichment data to indicate a $C \propto 1/d^2$ relationship.
3. Bubble bursting at high temperatures as a source of fine particles with compositions similar to the large-particle parents (Ramsden, 1969; Smith et al., 1979b). No quantification of particle size distribution resulting from bubble bursting has been made. Conclusive evidence for this mechanism is yet to be provided.

These mechanisms may now be compared with some of the available data regarding mass-size distribution and elemental-size distribution.

PARTICLE SIZE DISTRIBUTION

Measurement Techniques

The measurement of aerosol size distributions should be reviewed before examining the data and comparing them to theories. The study of experimental techniques is still a research activity. Major problems with measurements and data analysis include these:

a. In situ cascade impactors have limited resolution of particle populations greater than 10 μm because of wall and inlet nozzle losses (Cushing et al., 1976; Knapp, 1980). Lower cutpoint is usually limited to about 0.2 μm. Impactors may have problem with particle bounce and reentrainment, which is especially serious for lower range of cut sizes.
b. Extractive sampling to condition stack gas for measurement by electrical aerosol analyzers (EAA) and optical particle counters introduces a bias in the particles larger than 1 μm. Also, a large dilution of stack gas sample is necessary to use these instruments. The EAA data for combustion aerosol should be corrected for cross sensitivities of neighboring channels (Markowski et al., 1980). The sharpness of the submicron mode *may* also be affected by coagulation within the sampling probe.

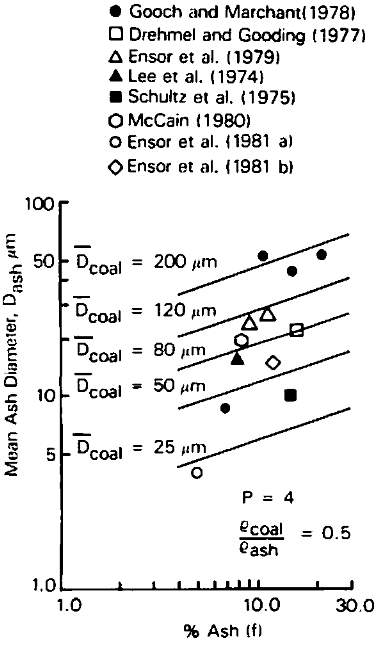
In general, conventional impactors are best suited for the size range of 0.5–10 μm, whereas EAA has better resolution in the submicron range. Diffusion batteries have also been used (McCain et al., 1975) for submicron ash analysis, but this instrument does not have cutpoints that are as sharp as those of EAA. The smallest cutpoint diameter of an impactor may be lowered further by operating the impactor under subatmospheric pressures. Particles as small as

0.02 μm can be impacted under partial vacuum because resistance from air molecules is reduced (Pilat, 1978; Flagan, 1981). This technique was successfully used by Ensor et al. (1981b) for field experimental evaluations and in the laboratory by Flagan and Taylor (1980).

Coarse Ash Fraction

Available data indicate that the majority of fly ash is above 1 μm in size with a broad peak in the range of 3–50 μm diameter. The actual mass mean diameter and shape of the size distribution depend upon several factors, such as coal type and composition and coal-particle size distribution. The large diameter mode may be called a *fly ash mode* and is generally explained by the breakup model, with P being the number of fragments produced per coal particle as a variable parameter. Laboratory data by Sarofim et al. (1977) indicate that P ranges from 3 to 5. With this model the mean ash diameter is given by Eq. (1). In Figure 5 the literature data on coal ash concentration and mean particle diameter are compared to curves predicted with Eq. (1) (Ensor, 1980). The value of P was assumed to be 4 and ρ_c/ρ_a to be ~0.5. Since all the data correspond to pulverized coal-fired systems, the mean coal particle diameter is expected to be ~80 μm. Only fair agreement with the model is seen. Several reasons are believed to contribute to the differences.

FIGURE 5. Mean fly ash particle diameter for uncontrolled sources as a function of coal ash mass fraction.



1. The accuracy of impactor measurements in determining ash size distribution may not be sufficient. Usually data are truncated at 10 μm and extrapolated assuming a log-normal distribution. This approximation can lead to large errors in mean ash diameter.
2. The coal size distribution is usually not known accurately at the time of the impactor measurements.
3. Usually some mass fraction of the ash is composed of cenospheres (up to 5%). Since these are large particles with lower density, a bias in the ash size distribution may be introduced.
4. The parameter P is assumed to be constant for all coal particle sizes. However, it may be a function of coal size and type. For a given coal type, the mean ash diameter may be reasonably expected to depend on mean coal particle size.
5. Morphological analysis of a coal flyash sample by Fisher et al. (1978) indicated 11 major classes of fly ash particles. The breakup model, on the other hand, predicts only particles of similar physical and chemical nature.

Submicron Ash Fraction

Submicron ash usually makes up less than 2% of the total fly ash mass. The lowest cutpoint diameter of a conventional cascade impactor is about 0.2 μm. With a low pressure impactor the cutpoint diameter can be lowered up to 0.02 μm (Ensor et al., 1981b; Flagan and Taylor, 1980), but the quantity collected on submicron stages is usually too small to weigh accurately. As a result, an impactor has limited sensitivity in the submicron range. Much better sensitivity in the submicron range is obtained by an EAA or a diffusion battery technique.

A distinct submicron mass mode was observed around 0.1 μm diameter when these instruments were used for analysis. McCain et al. (1975) found a broad submicron peak in number distribution by taking measurements with a diffusion battery. The peak reported by McCain disappears when size distribution is plotted on a mass basis. Sharper submicron peaks were observed when measurements were made by an EAA (Schmidt et al., 1976; Ensor et al., 1979; Flagan and Taylor, 1980; Markowski et al., 1980). These data retained the peaks when plotted on a mass basis. Peaks are especially sharp when the data reduction process takes into account cross sensitivities of neighboring channels of the EAA (Markowski et al., 1980). Ondov et al. (1979b) analyzed the impactor filter samples with scanning electron microscopy (SEM) and detected a mode at 0.16 μm. Particles were sized and counted from SEM photographs for this purpose.

These observations tend to support qualitatively the vaporization–condensation mechanism that predicts a submicron mode at 0.1 μm due to coagulation. When the observed number concentration of submicron particles from field measurements is compared with theoretical predictions, one or two orders of magnitude discrepancies are seen (Figure 4). The agreement is much better for the laboratory data taken by Flagan and Taylor (1980). Part of the discrepancies in field measurements may be explained by coagulation in the sampling probe. The difference in the submicron distribution data by Ensor et al. (1979, 1981a, b) taken with similar equipment and procedures at various sites indicates a strong influence of coal composition on the magnitude of the submicron distribution peak. Site-dependent variability was reported by McElroy et al. (1982).

ELEMENTAL SIZE DISTRIBUTIONS

Measurement Techniques

Several analytical techniques have been developed for the elemental analysis of a sample and have been summarized by Smith (1980). The most commonly used techniques are

1. x-ray fluorescence analysis (XRF),
2. instrumental neutron activation analysis (INAA),
3. atomic absorption analysis (AAA), and
4. x-ray photoelectron spectroscopy (ESCA).

The first three (XRF, INAA, and AAA) analyze bulk or volume samples, whereas ESCA analyzes the surface. A sputter-etching technique is normally used to remove surface layers of different depths and to expose internal material.

Sample preparation for analysis is of course an important step. Size-classified samples are required to determine elemental size distributions and concentrations. Most commonly, samples are collected on cascade impactor stages for later analysis for chemical compositions. In this scheme a filter collects all particles below the cutpoint of the last impaction stage, usually 0.2 μm. With the low pressure impactor it has been possible to collect samples of particles down to 0.02 μm; however, only limited data using this technique are available (Ensor et al., 1981b). Since the low pressure impactor has a larger number of stages, the possibility of contamination due to larger particles bouncing off from preceding stages is minimized. In a conventional impactor, with fewer stages and a lowest cutpoint diameter of 0.2 μm, the larger particles bouncing off from earlier stages are likely to contaminate the submicron fraction collected on the filter.

Impactor sampling provides in situ samples. Some analyses have also been made on bulk fly ash samples collected by control equipments. This ash was later size classified by techniques such as elutriation to provide samples for elemental analysis (Ondov et al., 1978; Desrosiers et al., 1979; Smith et al., 1979b). This scheme has been controversial. This procedure would work well provided there are no physical or chemical changes in accumulation and redispersion of the fly ash samples. This is probably the case for larger particle sizes. For small particles, however, particle interactions are expected to become significant. Upon collection and accumulation, small particles are likely to agglomerate among themselves to form larger ones; they also may adhere to larger particles. The smaller the particle is, the more energy that is required to separate it. With higher energy abrasion of large particles, the generation of "new" fine particles may become significant. Thus redispersion of collected fly ash, especially of the fine fraction, may introduce some measurement artifacts.

Data Analysis

Elemental size distribution data are only recently being investigated, and the techniques are still in experimental stages. The limited amount of data therefore understandably shows variations (e.g., Klein et al., 1975; Block and Dams, 1976).

Some broad generalizations may be made from the data obtained on coal-fired utility boilers. Most of the mass of ash is composed of so-called aluminosilicate matrix elements. These include Al, Si, Ca, Mg, and Fe. Na, K, and Ti are also usually present in significant quantities. The proportions of each of these elements depends on the coal type used. These elements are generally found in all size fractions, including submicron fractions, in similar proportions.

Most of the data show distinct enrichments of trace elements– As, Se, Sb, Zn, Mo, Pb, Ga, and Cd—in the finer size fractions. Enrichment has also been reported for W, but the data are limited. These may be called group I elements. A second group of elements may be made which show slight depletion or no change in elemental concentration with respect to particle size. These include Al, Si, Fe, Ca, Ti, Mg, K, Ce, Hf, and other rare-earth elements. A third grouping of elements includes those that show slight enrichment or intermediate undeterminable behavior. Also included in this group are those elements for whom conflicting trends have been reported. The group III elements include Ba, Sr, Ni, Cr, Co, Mn, Na, U, and V.

These groupings have been made to indicate general trends. Unusual behaviors have also been reported, e.g., slight enrichment of Ca (Ondov et al., 1979a), slight enrichment of Fe (Smith et al., 1979a), no change with Zn and Ga (Gladney et al., 1976), enrichment of Ti (Ondov et al., 1979b), depletion of Fe and of Ce relative to Al (Gladney et al., 1976), etc. These observations and the conflicting reports for group III elements may be the effect of coal type, different operating parameters (such as combustion temperature), and inaccuracies involved in sampling and analytical procedures.

Strong evidence of surface enrichments attributable to evaporation of volatile species followed by heterogeneous condensation have been found by Linton et al. (1976), Smith et al. (1979a, b), Hansen and Fisher (1980), Neville et al. (1981), and several other investigators. Since small particles have higher surface area-to-volume ratio, the enrichment is expected to increase with decreasing particle size. From simple geometrical considerations, Davison et al. (1974) proposed that the enrichment concentration of volatile species should be proportional to $1/d$, where d is fly ash particle diameter. For the continuum regime, condensation indicates $c \propto 1/d^2$ (Flagan and Friedlander, 1978). Flagan found that both relations fit reasonably well to data by Davison et al. (1974). Biermann and Ondov (1980) found better agreement with the $1/d^2$ relationship when data are taken with a cascade impactor of high resolution in the submicron range. Data taken with a conventional cascade impactor are usually available only to 0.2 μm. Extrapolation of the above relationship to the finer size range may be potentially misleading as it would predict a rapid increase in surface concentrations for every volatile element. Such extrapolations by Biermann and Ondov (1980) show that a particle of pure condensed material would have a diameter of 0.045 μm. The data taken with a low pressure cascade impactor (with a smallest cutpoint diameter of 0.02 μm), on the other hand, indicated an absence of particles below 0.08 μm (Ensor et al., 1981b).

Contrary to findings by Biermann and Ondov (1980) and others, data by Smith et al. (1979a, b) indicate the concentration of most of the volatile species in size fractions smaller than 1 μm to be independent of size. There is definite enrichment of volatiles in these particles compared with their concentration in larger particles. The concentrations have been shown to increase as the particle size decreased from 10 to 1 μm, where it levels off. These data were obtained by separating hopper ash, instead of in situ impactor sampling as used by several other researchers (Ensor et al., 1979, 1981 a, b; Biermann and Ondov, 1980). This discrepancy may be explained as measurement artifacts, as discussed earlier. Smith et al. (1979b) suggest bursting of bubbles as a possible mechanism for the formation of such fine particles.

The effect of matrix structure and surface segregation was pointed out by Stinespring and Stewart (1981). They showed that, at the elevated temperatures experienced during and after the combustion process, diffusive transport of the trace and minor elements to the surface of the ash particles (i.e., surface segregation) could contribute to the observed surface enrichment. Such processes require residence times of several hours at elevated temperatures to be significant in combustion processes. However, such processes may be possible after collection and deposition of fly ash particles or in advanced combustion processes utilizing fluid beds.

A common observation in the majority of the field data is the presence of relatively less volatile major matrix elements in the fine submicron fractions. These are seen even in the nearly monodisperse submicron modes observed by Ensor et al. (1979, 1981b). A submicron mass mode is qualitatively explained by the vaporization-condensation mechanism, as discussed earlier. However, the submicron mode may also be expected to be considerably depleted in less volatile species. To explain the presence of less volatile species like Al and Si in submicron fractions, a reduction of the refractory species Al_2O_3, SiO_2, and MgO to more volatile reduced species AlO, SiO, and Mg in the reducing zone near the burning particle surface has been suggested (Sarofim et al., 1977; Desrosiers et al., 1979; Mims et al., 1979; Neville et al., 1980). The vaporized reduced species may later oxidize in the oxidizing gas atmosphere away from the particle. The oxidized species would then condense out, because of their low volatility. To predict resulting submicron ash composition, kinetic data related to the listed reactions and thermodynamic data related to all compounds involved are needed. Such predictions, made by Ulrich et al. (1977) for a cyclone coal-fired boiler ash, were compared with experimental fly ash composition. Considerable discrepancies regarding Al_2O_3, CaO, and FeO compositions were observed and were attributed to the mixing of two sets of fine ash particles, one originating by vaporization-condensation and the other having composition similar to large particles and entrained by some other mechanism (Desrosiers et al., 1979). It may be pointed out that the presence of major matrix elements in submicron ash may also arise simply as an artifact of sampling technique, e.g., larger particles bouncing off impactor stages onto the filter.

Based on the vaporization mechanism, the relative volatilities of the species in the three groups may be expected to be in the following order:

group I > group III > group II.

Such an order, however, does not follow the expectations based on the volatility data of pure species or compounds. (Table 3 gives the boiling points of the elements and their compounds.) For example, Mg and K from group II are relatively more volatile than Ba, Sr, or Mn of group III. Also, it appears that for some species their specific chemical compounds need to be formed to justify their relative high volatility. Thus, for Ni and Mo, their carbonyls appear to be the volatilizing species. Halides seem to be the choice for U, V, Co, Cr, Sb, and Mn. The lower volatilities experienced by Na, K, and Mg may perhaps be explained if they are considered to be structurally incorporated into an aluminosilicate matrix structure.

Laboratory studies under controlled conditions by Sarofim et al. (1977) and by Flagan and Taylor (1980) show much different results compared with field studies regarding the behavior of major matrix elements. The role of evaporation and submicron ash composition were clearly shown to be a function of tempera-

TABLE 3. Boiling Points of Elements and Their Compounds

Species	Boiling point (°C)
As	613 (sublimes)
Se	685
Sb	1750
$SbCl_3$	283
Zn	907
ZnO	>2500
Mo	4612
$Mo(CO)_6$	156
MoO_3	1155 (sublimes)
Cd	765
Pb	1740
Al	2467
Al_2O_3	2980
Ca	1484
CaO	2850
Si	2355
SiO	1880
SiO_2	2230
Ti	3287
$TiCl_4$	136
Mg	1090
MgO	3600
K	774
Ba	1640
BaO	>2000
Sr	1384
SrO	>3000
Ni	2732
NiO	>3000
$Ni(CO)_4$	43
Cr	2672
Cr_2O_3	4000
CO	2870
CoO	>2000
Mn	1962
$MnCl_2$	1190
Na	883
U	3818
UCl_4	792
V	3380
VCl_4	148

From Perry and Chilton (1973).

ture and reflect the effect of reaction kinetics and relative volatilities of the species (Mims et al., 1979; Neville et al., 1980). More volatile Mg, Fe, and Na were considerably enriched, and Al and Ca were correspondingly depleted. Results with Si analysis indicated dependence upon coal type and structure. The nature and chemical composition of mineral species were found to effect its reactivity and volatility. The work of Flagan and Taylor indicated a large percentage of soot (unburned carbon), as well as sulfur in the submicron mode. The high concentration of Si in submicron fractions observed in these laboratory studies may be explained by formation of more volatile SiO near the particle surface because of the presence of reducing conditions. The submicron size distribution observed in Flagan and Taylor's work is in good agreement with that predicted by vaporization–homogeneous condensation mechanism. Thus the laboratory studies tend strongly to support the vaporization–condensation model for submicron particle formation.

CONCLUSIONS

(1) The formation of fly ash particles larger than 1 μm is reasonably explained by coal-particle breakup and the coalescence of molten grains of mineral matter during combustion. Cenospheres caused by inflation of the molten ash depend on the ash viscosity, but in most circumstances it is only a small fraction of the total ash on a weight basis. Laboratory data suggest the parameter P in the breakup model (indicating number of ash particles formed per coal particle) to be between 3 and 5. The data obtained from commercial coal-fired boilers show only moderate agreement with the model. This discrepancy may be primarily due to the difficulty in obtaining accurate particle size distributions above 10 μm in field tests.

(2) The physical particle size distribution in the less than 1 μm range is qualitatively explained by a vaporization–homogeneous condensation mechanism. The most likely explanation of the submicron mode observed in various field and laboratory data is vapor-to-particle conversion. Also, the concentration variability of submicron particles is indicative of a temperature and coal composition dependence. The concentration of submicron particles determined in field measurements on commercial scale boilers is, however, lower, often by two

orders of magnitude, than the laboratory measurements and theoretical predictions. Part of the explanation may be the coagulation of the submicron material in the sampling systems used in field tests. However, some of the field-size distributions (Ensor et al. 1981a) obtained with equipment designed to minimize coagulation did not appear to be significantly different than the other field data.

(3) The elemental size distribution from field measurements on commercial scale boilers indicates that the ash is mostly composed of so-called aluminosilicate major matrix elements. These are generally found in all size fractions, including submicron fractions, in similar proportions. These observations are not consistent with a simple vaporization–homogeneous nucleation model for submicron particle formation. Alternative mechanisms suggested for the formation of such fine particles containing aluminosilicate matrix elements include (a) the presence of extraneous submicron particles not associated with coal such as clays, (b) mineral inclusions released as submicron particles without coalescence (c) the bursting of molten ash bubbles releasing fine submicron particles, and (d) the reduction of matrix elements at the coal particle surface during combustion, producing more volatile species.

The laboratory studies with controlled combustion conditions indicate a greater concentration particle size dependence for major matrix elements than reported from field tests. The laboratory results are consistent with the vaporization homogeneous condensation mechanism, with the enrichment and depletion of a species depending on its relative volatility. The enrichment of silicon in fine-size fractions is considered to be due to formation of volatile SiO in the reducing atmosphere near the coal-particle surface, while aluminum is depleted in the fine-size fractions. The elemental size distributions are also found to depend on coal composition. The laboratory particle separation experiments have been conducted under conditions to minimize measurement artifacts introduced by impactors, which may have been significant in field tests.

(4) The observed particle surface enrichment by trace volatile species over the whole size range is generally explained by a vaporization–heterogeneous condensation mechanism. The enrichment is especially dominant in fine-size fractions owing to their higher surface area to volume ratio compared to coarse size fractions. The concentration of trace species increases with decreasing particle size and is found to vary as $1/(\text{particle diameter})^2$ with reasonable accuracy for limited data.

REFERENCES

Babcock and Wilcox (1978). *Steam/Its Generation and Use*, 39th ed., New York.

Biermann, A. H., and Ondov, J. M. (1980). Applications of surface-deposition models to size-fractionated coal fly ash, *Atmos. Env.* 14:289–295.

Block, C., and Dams, R. (1976). Study of fly ash emission during combustion of coal, *Environ. Sci. Technol.* 10:1011–1017.

Burchard, J. K. (1974). The significance of particulate emissions, *J. Air Poll. Control Assoc.* 24:1140–1142.

Cushing, K. M., Lacey, G. E., McCain, J. D., and Smith, W. B. (1976). Particulate sizing techniques for control device evaluation: Cascade impactor calibration, EPA Rep. 600/2-76-280, October.

Davison, R. L., Natusch, D. F. S., Wallace, J. R., and Evans, C. A., Jr. (1974). Trace elements in fly ash dependence of concentration on particle size, *Eviron. Sci. Technol.* 8:1107–1113

Desrosiers, R. E., Riehl, J. W., Ulrich, G. D., and Chiu, A. S. (1979). Submicron fly ash formation in coal fired boilers, *Proc. 17th symp. Combust., Combust. Inst.*, 1395–1403.

Drehmel, D. C., and Gooding, C. H. (1977). Field tests of a hot-side electrostatic precipitator. Proceedings: particulate collection problems using ESPs in the metallurgical industry, EPA Rep. 600/2-77-208, October.

Ensor, D. S., Cowen, S., Hooper, R., Markowski, G., Scheck, R., Farrell, J. D., and Burnham, J. (1979). Evaluation of the george meal No. 3 electrostatic precipitator, EPRI Rep. FP-1145, August.

Ensor, D. S. (1980). Stationary source aerosol emissions, presented Symp. Plume and Visibility: Measurements and Model Components, Grand Canyon, AZ, November.

Ensor, D. S., Lawless, P. A., Damle, A. S., and Sparks, L. E. (1981a). Evaluation of the United McGill electrostatic precipitator, presented at the EPA 3rd Symp. Transfer and Utilization of Particulate Control Technology, Orlando, FL, March.

Ensor, D. S., Cowen, S., Shendrikar, A., Markowski, G., Woffinden, G., Pearson, R., and Scheck, R. (1981b).

Kramer station fabric filter evaluation. EPRI Rep. CS-1669, January.

Finkelman, R. B. (1970). Determination of trace element sites in the Waynesburg by SEM analysis of accessory minerals, *Scanning Electron Microscopy* 1:60.

Fisher, L. L., Prentice, B. A., Iberman, D. S., Ondov, J. M., Bierman, A. H., Ragaini, R. C., and McFarland, A. R. (1978). *Environ. Sci. Technol.* 12:447–451.

Flagan, R. C. (1979). Submicron particles from coal combustion, *Proc. 17th Symp. Combustion, Combustion Inst.*, 97–104.

Flagan, R. C. (1981). Temperature and pressure effects in low pressure cascade impactors, presented at ACS-81 Winter Symp. Aerosol Sci. Tucson, AZ, January.

Flagan, R. C., and Friedlander, S. K. (1978). Particle formation in pulverized coal combustion—a review, in *Recent Developments in Aerosol Science* (D. T. Shaw, ed.), Wiley, New York, Ch. 2.

Flagan, R. C., and Taylor, D. D. (1980). Laboratory studies of submicron particles from coal combustion, *Proc. 18th Symp. Combustion, Combustion Inst.*, 1227–1237.

Gladney, E. S., Small, J. A., Gordon, G. E., and Zoller, W. H. (1976). Composition and size distribution of in-stack particulate material at a coal-fired power plant, *Atmos. Environ.* 10:1071–1077.

Gluskoter, H. J., Ruch, R. R., Miller, W. H., Cahill, R. W., Dreher, G. B., and Kuhn, J. K. (1977). Trace elements in coal: Occurence and distribution, EPA Rep. 600/7-77-064, June.

Gluskoter, H. J., Shimp, N. F., and Ruch, R. R. (1981). Coal analyses, trace elements, and mineral matter, in *Chemistry of Coal Utilization* (M. A. Elliott, ed.), Wiley, New York, Ch. 7.

Gooch, J. P., and Marchant, G. H. (1978). Electrostatic precipitator rapping reentrainment and computer model studies, EPRI Rep. FP-792.

Green, H. L., and Lane, W. R. (1964). *Particulate Clouds: Dust, Smokes and Mists*, 2nd ed., Van Nostrand Reinhold, New York.

Hansen, L. D., and Fisher, G. L. (1980). Elemental distribution in coal fly ash particles, *Environ. Sci. Technol.* 14:1111–1117.

Kaakinen, J. W., Jorden, R. M., Lawasani, H. H., and West, R. E. (1975). Trace element behavior in coal-fired power plant, *Environ. Sci. Technol.* 9:862–869.

Klein D. H., Andren, A. W., Carter, J. A., Emery, J. F., Feldman, C., Fulkerson, W., Lyon, W.S., Ogle, J. C., Talmi, Y., Van Hook, R. I., and Bolton, N. (1975). Pathways of thirty-seven trace elements through coal-fired power plant, *Environ. Sci. Technol.* 9:973–979.

Knapp, K. T. (1980). The effects of nozzle losses on impactor sampling, Paper 6, Proc. Advances in Particle Sampling and Measurement, EPA Rep. 600/9-80-004, January.

Lee, R. E., Crist, H. L., Riley, A. E., and McLeod, K.E. (1974). Concentration and size of trace metal emissions from a Power Plant, a steel plant, and a cotton gin, *Environ. Sci. Technol.* 9:643–647.

Levenspiel, O. (1962). *Chemical Reaction Engineering*, Wiley, New York.

Linton, R. W., Loh, A., Natusch, D. F. S., Evans, C. A., and Williams, P. (1976). Surface predominance of trace elements in airborne particles, *Science* 191:852–854.

Markowski, G. R., Ensor, D. S., Hooper, R. G., and Carr, R. C. (1980). Submicron aerosol mode in flue gas from a pulverized coal utility boiler, *Environ. Sci. Technol.*, 14:1400–1402.

McCain, J. D., Gooch, J. P., and Smith, W. B. (1975). Results of field measurements of industrial particulate sources and electrostatic precipitator performance, *J. Air Poll. Control Assoc.* 25:117–121.

McElroy, M. W., Carr, R. C., Ensor, D. S., and Markowski, G. R. (1982). Size distribution of fine particles from coal combustion, *Science* 215:13–49.

Mims, C. A., Neville, M., Quann, R. J., and Sarofim, A. F. (1979). Laboratory studies of trace element transformation during coal combustion, paper No. 78, presented 87th AIChE Meeting, August.

Neville, M., Quann, R. J., Haynes, B. S., and Sarofim, A. F. (1980). Vaporization and condensation of mineral matter during pulverized coal combustion, presented at 18th Symp. Combust., Waterloo, Canada, August.

Neville, M., Quann, R. J., Haynes, B. S., and Sarofim, A. F. (1981). Factors governing the surface enrichment on fly ash of volatile trace species, presented at the ACS/IEC Winter Symp., Tucson, AZ, January.

Ondov, J. M., Ragaini, R. C., Biermann, A. H. (1978). Elemental particle-size emissions from coal-fired power plants: Use of an internal cascade impactor, *Atmos. Environ.* 12:1175–1185.

Ondov, J. M., Ragaini, R. C., and Biermann, A. H. (1979a). Emissions and particle size distributions of minor and trace elements at two western coal-fired power plants equipped with cold-side electrostatic precipitators, *Environ. Sci. Technol.* 13:946–953.

Ondov, J. M., Ragaini, R. C., and Biermann, A. H. (1971). Elemental emissions from a coal-fired power plant. Comparison of a Venturi wet scrubber system with a cold-side electrostatic precipitator, *Environ. Sci. Technol.* 13:598–607.

Perry, R. H., and Chilton, C. H. (1973). *Chemical Engineers' Handbook*, 5th ed., McGraw Hill, New York.

Pilat, M. J. (1978). Development of a cascade impactor system, EPRI Project Rep. FP-844, August.

Ramsden, A. R. (1969). A microscopic investigation into the formation of fly ash during the combustion of a pulverized bituminous coal, *Fuel (London)* 48:121–237.

Sarofim, A. F., Howard, J. B., and Padia, A. S. (1977). The physical transformation of the mineral matter in pulverized coal under simulated combustion conditions, *Combust. Sci. Technol.* 16:187–204.

Schmidt, E. W., Gieseke, J. A., and Allen, J. M. (1976). Size distribution of fine-particulate emissions from a coal-fired power plant, *Atmos. Environ.* 10:1065–1069.

Schultz, E. J., Engdahl, R. B., and Frankenberg, T. T.

(1975). Submicron particles from a pulverized coal-fired boiler, *Atmos. Enviorn.* 9:111–119.

Shannon, L. J. (1974). Control technology for fine particulate emissions, EPA Rep. 650/2-74-027, May.

Smith, R. D. (1980). The trace element chemistry of coal during combustion and the emissions from coal-fired plants, *Progr. Energy Combust. Sci.* 6:53–119.

Smith, R. D., Campbell, J. A., and Nielson, K. K. (1979a). Concentration dependence upon particle size of volatilized elements in fly ash, *Environ. Sci. Technol.* 13:553–558.

Smith, R. D., Campbell, J. A., and Nielson, K. K. (1979b). Characterization and formation of submicron particles in coal-fired plants, *Atmos. Environ.* 13:607–617.

Stinespring, C. D., and Stewart, G. W. (1981). Surface enrichment of aluminosilicate minerals and coal combustion ash particles, *Atmos. Environ.* 15:307–313.

Swanson, V. E., Medlin, J. H., Hatch, J. R., Coleman, S. L., Wood, G. H., Woodruff, S. D., and Hildebrand, R. T. (1976). Collection, chemical analysis, and evaluation of coal samples in 1975, U.S. Geol. Survey Rep. 76-468.

Tomaides, M., and Whitby, K. T. (1975). Generation of aerosols by bursting of single bubbles, presented at Symp. Fine Particles, Minneapolis.

Ulrich, G. D., Riehl, J. W., French, B. R., and Desrosiers, R. E. (1977). Mechanism of submicron fly-ash formation in a cyclone, coal-fired boiler, ASME Int. Symp. Corrosion and Desposits from Combustion Gases, Henniker, NH, June.

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Trace Elements in Fly Ash

Dependence of Concentration on Particle Size

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■ The concentrations of 25 elements in fly ash emitted from a coal-fired power plant have been measured as a function of particle size using spark source mass spectroscopy, optical emission spectrography, atomic absorption spectroscopy, and X-ray fluorescence spectroscopy. Of these elements, the concentrations of Pb, Tl, Sb, Cd, Se, As, Zn, Ni, Cr, and S were found to increase markedly with decreasing particle size. A mechanism involving high-temperature volatilization of a species containing the trace element followed by preferential condensation or adsorption onto the smallest particles is proposed to account for the trace element concentration dependence on particle size. The environmental significance of the results is discussed.

It is now well established that many high-temperature combustion and smelting operations emit particles containing toxic elements such as Be, Cd, As, Se, Pb, Sb, Hg, Tl, and V into the atmosphere (*1*). Many of these elements are enriched in ambient urban aerosols by as much as 100- to 1000-fold over their natural crustal abundance (*2*). Furthermore, most of their mass is concentrated in the particle size range 0.5–10.0 μm, which is inhaled and deposited in the human respiratory system.

A number of workers (*3–5*) have shown that inhaled airborne particles are deposited in different regions of the body depending on their aerodynamic size. This behavior is illustrated for three compartments of the respiratory system (*5*) in Figure 1. From a toxicological standpoint, the smallest particles (<1 μm) which deposit in the pulmonary region of the respiratory tract are of greatest concern. This is because the efficiency of extraction of toxic species from particles deposited in the pulmonary region is high (60–80%) (*1, 4, 6–8*), whereas the extraction efficiency from the larger particles, which deposit in the nasopharyngeal and tracheobronchial regions and are removed to the pharynx by cilial action and swallowed, is low (5–15%). Consequently, toxic species, which predominate in submicrometer-sized particles, will have their entry to the bloodstream enhanced over those which predominate in larger particles.

In fact, a number of toxic elements including Pb, Se, Sb, Cd, Ni, V, Sn, and Zn in urban aerosols have been reported to have equivalent mass median diameters of the order of 1 μm or less, which is considerably less than those reported for common matrix elements such as Fe, Al, and Si. Mass median diameters of these elements lie in the range of 2.5–7.0 μm (*9–12*). It is therefore meaningful to determine whether certain toxic elements predominate in the smallest particles emitted from particulate sources or whether the mass median diameter differences in urban aerosols are simply due to mixing of particles characteristic of individual source emissions.

The work reported here was designed to establish whether elements present in fly ash particles emitted from coal-fired power plants (essentially ubiquitous contributors to urban aerosols) exhibit a dependence of element concentration on particle size. A variety of analytical techniques was employed to choose the most reliable for the determination of individual elements in fly ash and to establish the data firmly.

Experimental

Sample Collection and Size Differentiation. Two types of samples are represented: (a) fly ash retained in the cyclonic precipitation system of a coal-fired power plant and (b) airborne fly ash collected in the ducting approximately 10 ft from the base of the stack. The retained material was collected in bulk and was size differentiated physically by sieving and aerodynamically in the laboratory with a Roller particle size analyzer (American Instrument Co.). Airborne fly ash samples were collected and size differentiated in situ using an Andersen stack sampler fabricated from stainless steel and designed to operate at the stack temperature. Although results are reported for samples collected in a single plant, the trace element content of fly ash collected in this plant equipped with cyclonic precipitators and using southern Indiana coal was shown to be representative of that in eight U.S. power plants utilizing a variety of coal types.

Particle size calibrations were based on the data supplied by the manufacturers of the analyzers employed. These data are established in terms of equivalence to the aerodynamic diameter of spherical particles of unit density (*13, 14*). Since fly ash particles are predominantly spherical, a rough check on the validity of the aerodynamic sizes can be obtained by determining the average physical size of particles in a given size fraction. For this pur-

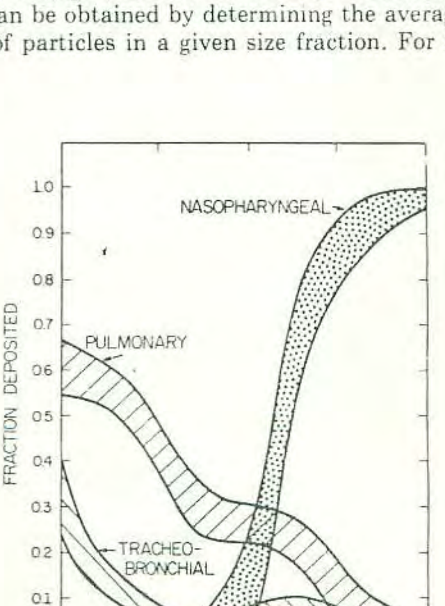

Figure 1. Efficiency of particle deposition in the three respiratory system compartments (*5*)

pose, particles collected on the third and fourth plates (4.6-7.1 μm and 3.0-4.6 μm equivalent aerodynamic diameter) of the Andersen stack sampler were examined using a Coulter counter (Coulter Electronics Inc., Hialeah, Fla.) in the timed analysis mode with a 100-μm aperture.

Milligram portions of the fly ash were dispersed in a 50% mixture of methanol in water and ultrasonically agitated for 5 min before adding the suspension to the counter. When we assumed a particle density of 2.5 g/cm^3 to convert volume median diameters to approximate aerodynamic diameters, values of 6.3 and 4.3 μm equivalent aerodynamic diameter were obtained. These indicate the general validity of the aerodynamic size calibration data.

In this experiment there was no evidence of particle diameter changing with time due to particle solubility in the methanol-water mixture. Indeed, none was expected since the particle matrices consist predominantly of insoluble aluminum and silicon and iron oxides, and soluble species are relatively minor constituents.

Analytical Procedures. The analytical methods employed fall into two classes, those which analyze the fly ash directly as the solid and those which analyze the sample in solution following wet digestion. The former methods retain sample integrity but involve calibration uncertainties: the latter allow easy calibration but are susceptible to possible formation of analytically intractable compounds during digestion.

Sample digestion was achieved by heating 0.5 gram of fly ash, 3.5 ml of 3:1 concentrated HCl/HNO_3 (aqua regia), 0.5 ml water, and 2.5 ml of an aqueous solution containing 48% HF for 2 hr at 110°C in a 25-ml Teflon-lined Parr pressure bomb (Parr Instrument Co., Moline, Ill.). After it cooled, 2.5 grams of boric acid were added to neutralize the HF. The small amount of black solid residue remaining was removed by centrifugation and was shown by spark sources mass spectrometry to contain mainly Ca, F, and Al in addition to carbon. At least 95% extraction of the elements of interest was achieved.

Atomic absorption analyses were performed by direct aspiration of dilutions of the original digest for Pb, Tl, Cd, As, Ni, and Be. Air-acetylene flames were employed for all elements except Be for which nitrous oxide-acetylene was used. A Jarrel Ash 8-10 dual-beam double monochromator instrument was employed. Background corrections were achieved by monitoring a nonabsorbing wavelength within 40 Å of the analytical wavelength. Se was determined by its atomic absorption after conversion to volatile H_2Se according to the method of Schmidt and Royer (*15*). Standard addition calibrations were performed in all cases, and a precision of ±10% was achieved.

The elements Pb, Be, Cr, Mn, Co, and Ni were determined by dc arc emission spectroscopy using a Baird-Atomic 3-meter spectrograph. Samples coarser than 325 mesh (Tyler series) were ground to pass through a 325-mesh sieve. One part by weight of fly ash was mixed with four parts of spectroscopic graphite for 1 min in a Wig-L-Bug mechanical shaker (Spex Industries). Spex mix A-7 pure graphite standards doped with 49 elements were used for comparative standards. Approximately 50 mg of graphite diluted sample were burned to completion in a cup electrode operating with a 4-mm gap and 10-amp current. Element concentrations were obtained with a precision of ±30%.

The fly ash matrix elements Fe, Ti, Al, Si, Ca, K, S, and Mg were determined using a vacuum-path, single-crystal, Phillips X-ray spectrometer. All samples of nominal particle diameter >4 μm were ground further so as to minimize surface sampling and inhomogeneity effects. The powders were suspended in propanol and dispersed ultrasonically before deposition by filtration onto 0.4-μm millipore membrane filters (*16*). Mineral standards previously calibrated against NBS mineral standards were supplied by the Illinois State Geological Survey. K_α radiation was monitored for all elements and a vacuum radiation path maintained for all elements except Fe and Ti. A lithium fluoride crystal was employed for detecting Fe and Ti, EDDT was used for Al, Si, Ca, K, and S, and ADP was used for Mg. For this method, precisions of ±5% were achieved.

An AEI model MS-7 spark source mass spectrometer was used for the qualitative determination of all elements of atomic number greater than 11 and for quantitative determination of Bi, Pb, Tl, Sb, Sn, As, Zn, Cu, Ni, Fe, V, Ca, K, and Si. One part of fly ash was mixed by weight with two parts of spectroscopic graphite for 5 min in a Wig-L-Bug and the mixture pressed into an electrode. Electrodes were manually positioned and sparked using a 25-μsec spark duration and a repetition rate of 300 sec^{-1} at 10^{-6} torr source pressure. Mass spectra were recorded photographically.

Internal standardization of the mass spectra was achieved by referencing line intensities both to the Pb in the sample and to 60 μg/g of solution-doped Au. The Pb was determined independently by atomic absorption spectroscopy. The $^{197}Au^+$ ion was at least two orders of magnitude more intense than $^{181}Ta^{16}O^+$ from source contamination. Element concentrations were calculated from the expression by Farrar (*17*).

$$C_X = C_{St}\,\frac{I_X}{I_{St}}\left[\frac{M_X}{M_{St}}\right]^2\frac{\Phi_{St}}{\Phi_X}\,k \qquad (1)$$

where

I = peak intensity of ion beam
Φ = isotopic abundance
M = mass
C = concentration
k = sensitivity factor for a given element relative to the standard
St and X = internal standard and analyte quantities, respectively

This expression assumes that the line width on the photographic plate is proportional to $M^{1/2}$ (*18*). Values of k were determined by doping increasing amounts of Pb, Tl, Sb, Sn, As, and Ni into the graphite before forming a series of electrodes with fly ash. For these elements, values of k ranged from 1.0-1.8. For the remaining elements, k was set equal to unity, an assumption usually valid within a factor of three (*17*). Precisions of ±20% were achieved.

Carbon present as SiC, FeC, and free C was determined as CO_2 after combustion with O_2 on a V_2O_5 catalyst (*19*).

Results

Results of the fly ash analyses are listed in Tables I-III for the technique considered most reliable for each element. Sieved fly ash fractions are listed with physical diameters, but all other fractions are represented in terms of equivalent aerodynamic diameters. Fly ash particles larger than 74 μm (200 mesh, Tyler series) exhibited no dependence of element concentration on particle size so that the concentrations listed for this fraction are averages over all larger fractions.

The 25 elements are classified into three groups. In Table I are listed those elements exhibiting concentration increases with decreasing particle diameter. These concentration increases, which were well above experimental error and confirmed by at least two analytical techniques, were consistently observed in a range of samples and were present in the airborne fly ash collected from the ducting. Table II contains elements which showed concentration trends only in the retained or in the airborne particle size fractions or which, like V, Mn, and Be, exhibited nonuniform dependence on particle size. Table III contains elements which showed no convincing trends within our experimental errors.

It should be noted that some of the values listed in Tables I-III show considerable deviation from the apparent trends. Repeated analyses of duplicate samples indicate that such deviations are essentially random and are thus

Table I. Elements Showing Pronounced Concentration Trends

Particle diam, μm	Pb	Tl	Sb	Cd	Se	As	Ni	Cr	Zn	S, wt %	Mass fraction %
	μg/g										
A. Fly Ash Retained in Plant											
Sieved fractions											
>74	140	7	1.5	<10	<12	180	100	100	500	...	66.30
44–74	160	9	7	<10	<20	500	140	90	411	1.3	22.89
Aerodynamically sized fractions											
>40	90	5	8	<10	<15	120	300	70	730	<0.01	2.50
30–40	300	5	9	<10	<15	160	130	140	570	0.01	3.54
20–30	430	9	8	<10	<15	200	160	150	480	...	3.25
15–20	520	12	19	<10	<30	300	200	170	720	...	0.80
10–15	430	15	12	<10	<30	400	210	170	770	4.4	0.31
5–10	820	20	25	<10	<50	800	230	160	1100	7.8	0.33
<5	980	45	31	<10	<50	370	260	130	1400	...	0.08
Analytical method											
	[a]	[a]	[a]	[a]	[a]	[a]	[b]		[a]	[a]	
B. Airborne Fly Ash											
>11.3	1100	29	17	13	13	680	460	740	8100	8.3	
7.3–11.3	1200	40	27	15	11	800	400	290	9000	...	
4.7–7.3	1500	62	34	18	16	1000	440	460	6600	7.9	
3.3–4.7	1550	67	34	22	16	900	540	470	3800	...	
2.1–3.3	1500	65	37	26	19	1200	900	1500	15000	25.0	
1.1–2.1	1600	76	53	35	59	1700	1600	3300	13000	...	
0.65–1.1	...	...	...	...	...	...	...	...	...	48.8	
Analytical method											
	[d]	[a]	[a]	[d]	[d]	[d]	[d]	[d]	[a]	[c]	

[a] Dc arc emission spectrometry. [b] Atomic absorption spectrometry. [c] X-ray fluorescence spectrometry. [d] Spark source mass spectrometry.

Table II. Elements Showing Limited Concentration Trends

Particle diameter, μm	Fe, wt %	Mn, μg/g	V, μg/g	Si, wt %	Mg, wt %	C, wt %	Be, μg/g	Al, wt %
A. Fly Ash Retained in Plant								
Sieved fractions								
>74	...	700	150	...	...	...	12	...
44–74	18	600	260	18	0.39	11	12	9.4
Aerodynamically sized fractions								
>40	50	150	250	3.0	0.02	0.12	7.5	1.3
30–40	18	630	190	14	0.31	0.21	18	6.9
20–30	...	270	340	...	...	0.63	21	...
15–20	...	210	320	...	...	2.5	22	...
10–15	6.6	160	320	19	0.16	6.6	22	9.8
5–10	8.6	210	330	26	0.39	5.5	24	13
<5	...	180	320	...	...	...	24	...
Analytical method								
	[a]	[b]	[c]	[d]	[d]	[d]		[d]
B. Airborne Fly Ash								
>11.3	13	150	150	34	0.89	0.66	34	19.7
7.3–11.3	...	210	240	...	...	0.70	40	...
4.7–7.3	12	230	420	27	0.95	0.62	32	16.2
3.3–4.7	...	200	230	...	...	0.57	55	...
2.06–3.3	17	240	310	35	1.4	0.81	43	21.0
1.06–2.06	...	470	480	...	...	0.61	60	...
0.65–1.06	15	...	...	23	0.19	...	...	9.8
Analytical method								
	[d]	[b]	[c]	[d]	[d]	[e]	[b]	[d]

[a] Dc arc emission spectrometry. [b] X-ray fluorescence spectrometry. [c] Atomic absorption. [d] Spark source mass spectrometry. [e] Oxygen fusion.

attributed to poor sampling statistics, a result of the heterogeneous nature of fly ash. It is considered appropriate, however, to present raw data obtained for a coherent set of size fractions to illustrate this problem of sampling and to avoid possible biases in the data.

Discussion

The results presented in Tables I, II, and III demonstrate four significant points:

A coal-fired power plant produces enrichment of certain elements in the smallest emitted particles.

The highest concentrations of these trace elements are found in particles which deposit in the pulmonary region of the respiratory system.

Existing particle control devices are least effective for removing the most toxic particles.

Estimates of toxic element emissions based on analyses of undifferentiated fly ash collected from particle precipitators will be much lower than actual emissions.

In fact, only a small fraction of the total fly ash mass has particle diameters <10 μm (Table I) and by no means all of this is emitted to the atmosphere. However, the fraction emitted undoubtedly presents a greater potential health hazard per unit weight than that retained. Furthermore, the dependences of element concentration on particle size presented in Table I may be less pronounced than actually occurs. This is a result of the substantial overlap of size fractions deposited on different plates of the Andersen stack sampler (*20*).

Essentially similar dependence of element concentration on fly ash particle size has been obtained by Lee and von Lehmden (*21*) for Cd, Pb, Mn, and Cr and by Toca (*22*) for Pb and Cd. Toca also found that 70% of the Cd present in flue gases was associated with particles <5 μm in diameter. More recently, Sparks (*23*) reported that the elements Pb, Ba, Sr, Rb, As, and Zn in fly ash particles collected on a 0.4-μm millipore filter, following the last stage of a Brinks impactor, were enriched on a weight-for-weight basis by at least an order of magnitude over those deposited on the last impactor stage.

One explanation of the dependence of element concentration on particle size is that the ashing characteristics of pyritic inclusions that contain many of the trace elements (*24, 25*) predominantly give rise to small particles. However, we incline to the view that certain elements or their compounds are volatilized in the high-temperature coal combustion zone and then either condense or adsorb onto entrained particles. The mass deposited is thus greatest per unit weight for the smallest particles.

In support of this volatilization adsorption-condensation hypothesis, it is noteworthy that all the elements (except Cr and Ni) listed in Table I have boiling points comparable to or below the temperature of the coal combustion zone (1300–1600°C). This is also true of Ba, Sr, and Rb as determined by Sparks (*23*). This statement implies that metal compounds are reduced to the element before volatilization. However, while reduction in the combustion zone is certainly feasible, such reduction is not necessary to our basic hypothesis. Indeed, neither Ni nor Cr, both of which exhibit a marked dependence of concentration on particle size (Table I), would exist as stable vapors (Table IV). It is suggested that these elements have access to the vapor phase as sulfides or, conceivably, as carbonyls whose highly transient formation during coal combustion has been postulated (*1*). Mercury, of course, undoubtedly volatilizes as the element and is predicted to exhibit a dependence of concentration on particle size if the proposed mechanism is valid.

Additional support for the mechanism is provided by the work of Hulett (*26*). He has shown by scanning electron microscopic analyses of individual argon ion etched fly ash particles that Zn, Cr, and Ni (the most concentrated elements in Table I) predominate on particle surfaces.

A simple model can be constructed by considering a single particle in which an element, X, is uniformly deposited on the particle surface at a concentration C_S (μg/cm²). In addition, X is assumed to be uniformly distributed throughout the particle with a concentration C_o (μg/g). The total concentration of X, C_X (μg/g), is then given by

$$C_X = C_o + \frac{C_S A}{\rho V} \tag{2}$$

Table III. Elements Showing No Concentration Trends

Particle diameter, μm	Bi, μg/g	Sn, μg/g	Cu, μg/g	Co, μg/g	Ti, wt %	Ca, wt %	K, wt %
			A. Fly Ash Retained in Plant				
			Sieved fractions				
>74	>2	>2	120	28	. . .	. . .	. . .
44–74	>2	>2	260	27	0.61	5.4	1.2
			Aerodynamically sized				
>40	>2	>2	220	75	0.01	2.5	2.54
30–40	>2	>2	120	76	0.64	6.3	6.26
20–30	>2	>2	160	55	. . .	. . .	. . .
15–20	>2	>2	220	50	. . .	4.5	4.46
10–15	>2	>2	220	55	0.66	4.0	4.04
5–10	>2	>2	390	46	1.09	. . .	. . .
>5	>2	>2	490	54	. . .	. . .	. . .
			B. Airborne Material				
>11.3	>1.7	7	270	60	1.12	4.9	4.9
7.3–11.3	>3.5	11	390	85	. . .	. . .	. . .
4.7–7.3	>4.0	18	380	90	0.92	4.2	4.2
3.3–4.7	>4.8	19	. . .	95	. . .	. . .	. . .
2.06–3.3	>4.5	16	330	90	1.59	5.0	5.0
1.06–2.06	>4.4	18	300	130	. . .	. . .	. . .
0.65–1.06	. . .	. . .	. . .	. . .	1.08	2.6	2.6
			Analytical method				
	a	a	a	b	c	c	c

[a] Spark source mass spectrometry. [b] Dc arc emission spectrometry. [c] X-ray fluorescence spectrometry.

Table IV. Boiling Points of Possible Inorganic Species Evolved During Coal Combustion

Species boiling or subliming, <1550°C	Species boiling or subliming, >1550°C
As, As_2O_3, As_2S_3	Al, Al_2O_3
Ba	BaO
	BeO
Bi	Bi_2O_3
Ca	C
Cd, CdO, CdS	CaO
$Cr(CO)_6$, $CrCl_3$, CrS (155°)	Co, CoO, CoS
K	Cr, Cr_2O_3
Mg	Cu, CuO
$Ni(CO)_4$	Fe, Fe_2O_3, Fe_3O_4, FeO
$PbCl_2$, PbO, PbS	MgO, MgS
Rb	Mn, MnO, MnO_2
S	Ni, NiO
	Pb 1620–1750°C
Se, SeO_2, SeO_3	Si, SiO_2
Sb, Sb_2S_3, Sb_2O_3	Sn, SnO_2
	SrO
SnS	Ti, TiO_2, TiO
Sr	U, UO_2
Tl, Tl_2O, Tl_2O_3	
Zn, ZnS	ZnO

where

C_o = bulk concentration of X
C_S = surface concentration of X
C_X = total concentration of X
V = particle volume
A = particle surface area
ρ = particle density

By summing overall fly ash particles and assuming spherical particles, the average concentration of X, $\bar{C}_X$, is given by

$$\bar{C}_X = \bar{C}_o + \frac{6\bar{C}_S}{\bar{\rho}} \frac{1}{\bar{D}} \tag{3}$$

where D is the particle diameter and the bars denote average values. Microscopic observation does, in fact, show that most particles are spherical.

To substitute the values in Table I into Equation 3, it is necessary either to make the assumption that $\bar{\rho}$ is not a function of particle diameter, D, or to determine $\bar{\rho}$ for each size fraction. Appropriate values of D for each size fraction can be obtained by assuming

$$\bar{D} = \frac{(ECD)_u + (ECD)_l}{2} \tag{4}$$

where $(ECD)_u$ and $(ECD)_l$ are the upper and lower 50% cutoff diameters for each stage of the Andersen stack sampler. Equation 2 thus assumes a symmetrical distribution of the mass of X over the diameter range $(ECD)_u$ to $(ECD)_l$. Incorporating these assumptions enables construction of a plot of $\bar{C}_X$ vs. $\bar{D}^{-1}$ as depicted in Figure 2 from which it can be seen that the results are in at least qualitative agreement with the proposed model.

The thickness, l, of the deposition layer can then be estimated from the expression

$$l = \bar{C}_S/\bar{\rho}' \tag{5}$$

where $\bar{\rho}'$ is the density of the deposition layer which was assumed equal to 3 g/cm³. Values of $\bar{C}_S$, $\bar{C}_o$, and l are presented in Table V. These values, with the notable exception of those for sulfur, are considered reasonable for a thin surface-deposited layer. The 0.06 μm "layer thickness" obtained for sulfur is considered too great to be accounted for by a simple adsorption process. Indeed, the high concentrations of S obtained for the 0.65–1.1 μm size fraction (Table I) can only be accounted for if sulfur is present as the element. This suggestion is at variance with the findings of Hulett (27) who has shown, using electron spectroscopy, that S predominates as sulfate. We, therefore, consider that the sulfur values listed in Table I are all proportionately high owing to lack of a fly ash standard having sulfur deposited on the surface of appropriately sized particles, as required for our X-ray fluorescence analysis.

If the observed dependence of element concentration on particle size is, in fact, due to volatilization followed by adsorption or condensation, as is suggested, one would expect the same phenomenon to be exhibited by particles derived from all high-temperature solid combustion operations. Data for sources other than coal-burning power plants are not currently available to substantiate this suggestion but, if correct, it means that many sources may preferentially emit small particles high in toxic elements or their compounds. The mass median diameters of such elements in the emitted particle distribution will thus be reduced as a direct result of surface deposition. The extent of reduction can be determined by combining Equation 3 with the mass distribution function appropriate for a given particle source. In the case of a log-normal distribution, this gives the following:

$$\frac{dM_X}{d(\ln D)} = \frac{1}{\sqrt{2\pi}\,\ln\sigma_g}\left\{\bar{C}_o \exp\left[-\frac{(\ln D/D_g)^2}{2(\ln\sigma_g)^2}\right] + \frac{6C_S}{\bar{\rho}} \exp\left[\frac{(\ln\sigma_g)^2}{2}\right]\exp\left[-\frac{(\ln D/D_g + \ln^2\sigma_g)}{2\ln^2\sigma_g}\right]\right\} \tag{6}$$

where

σ_g = geometric standard deviation
M_X = mass of X
D_g = mass median diameter of original substrate distribution

Equation 6 does not provide a simple analytical expression for the mass median diameter of the adsorbed species, $D_g(X)$, except when C_o = 0—i.e., X is present only in the deposited layer. In this case, it can readily be shown (28) that

$$\ln D_g(X) = \ln D_g - \ln^2\sigma_g \tag{7}$$

Equations 6 and 7 demonstrate that the mass median diameter of a surface-deposited species, X, is considerably less than that of the total mass.

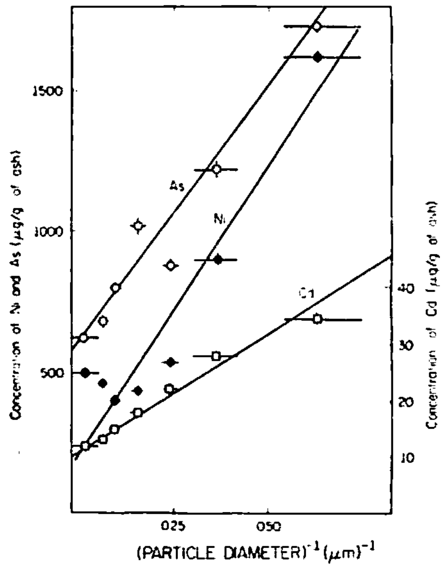

Figure 2. Dependence of element concentration on particle size for As, Ni, and Cd in fly ash emitted from a coal-fired power plant

Table V. Parameters Derived from Surface Deposition Model

Element	Sample pairs	C_s, μg/cm²	C_o, μg/g	Linear correlation coeff.	Estimated surface thickness, Å
Pb	6	0.04	1000	0.73	1.0
Tl	6	0.003	40	0.80	0.1
Sb	6	0.003	20	0.93	0.1
Cd	6	0.002	10	0.99	0.7
Se	6	0.004	0.7	0.92	0.1
As	6	0.009	600	0.97	0.3
Zn	6	0.6	6000	0.60	20
Ni	6	0.1	100	0.98	4.0
Cr	6	0.3	300	0.94	9.0
S	4	19.0	5 × 10	...	600

The validity of Equations 3 and 6 is destroyed as soon as particles from different sources become mixed into the ambient aerosol. However, if surface deposition is a widespread phenomenon as suggested earlier, one would expect volatile elements present in urban aerosols to have significantly lower mass median diameters than nonvolatile elements. In fact, data obtained by the National Air Suveillance Network (NASN) have shown the volatilizable elements Zn, Ni, Pb, Cd, and Ba to have statistically lower mass median diameters than common nonvolatilizable particle matrix elements. Also, although not substantiated statistically, Se and Sb have been shown to have small mass median diameters in ambient aerosols (*12*). Lead, of course, is not expected to be typical since it is derived mainly from a single source (the automobile) known to produce small particles.

The predominance of certain elements in small particles is also significant in determining the degree of enrichment of these elements in an urban aerosol, since the smallest particles have the longest atmospheric residence time. Indeed, Gladney et al. (*29*) have shown enrichment factors of greater than ten times over natural crustal abundance for Tl, Cr, Ni, Cu, Zn, As, Cd, Sn, Pb, Se, S, Cl, and Br in the Boston aerosol and have established substantial correlations with enrichment patterns in coal fly ash, municipal incinerator fly ash, and residual fuel oil. In the present context, it is noteworthy that the majority of these elements could be volatilized during combustion.

How

Although we have considered only trace elements present in particulate matter, the importance of vapor species such as SeO_2 and As_2O_3 should not be overlooked. Thermodynamic data (*30*) indicate that at 25°C as much as 80 $\mu g/m^3$ of Se as SeO_2 and 70 $\mu g/m^3$ of As as As_2O_3 can exist as vapors. These levels are much greater than normally observed for Se and As in urban aerosols (≤ 10 ng/m^3). It is possible, therefore, that additional amounts of these elements may be emitted as vapors. Consistent with this suggestion, Pillay and Thomas (*31*) have reported that at least 50% of the Se present in urban air passes through a filter designed to collect all particles greater than 0.1 μm in diameter. Comparable data are not available for As, but future sampling operations should undoubtedly undertake gaseous sampling procedures for both elements.

By employing a variety of analytical techniques in this study it has been possible to establish which are the most reproducible, precise, and interference free for individual elements in fly ash. Spark source mass spectrometry undoubtedly affords the greatest advantage for multielemental determination in solid fly ash although the analyses are extremely time consuming. In addition, interferences prevent the analysis of Te, Cd, Se, Co, Mn, Cr, and S and permit only a semiquantitative estimate for Be. Dc arc emission spectroscopy exhibits no significant advantages over spark source mass spectroscopy other than detection of Co, Mn, Cr, and Be and wider availability. The X-ray fluorescence method employed has the advantages of high speed and precision but is somewhat limited by calibration difficulties and matrix effects. The shallow penetration depths of soft X-rays from the lighter elements such as sulfur and magnesium necessitate high matrix identity between samples and standards and a very small particle size (*32*).

Atomic absorption spectrometry is considered to be the most accurate technique employed in this work. However, large amounts of samples are required if more than a few elements are determined. Also, great care must be taken to achieve good background corrections due to the large number of elements present. Atomic absorption spectrometry displayed no evidence of loss of sample integrity as a result of the fly ash digestion except, possibly, in the case of Tl where analyses were consistently 3–5 times lower than those obtained by spark source mass spectrometry and anodic stripping voltammetry after removal of the Pb interference. The reasons for this are being investigated.

Comparison of results obtained by different techniques has enabled confirmation of the size dependences represented in Tables I–III. The absolute values of concentrations obtained by different techniques are only in semiquantitative agreement. However, this is in accord with the findings of von Lehmden et al. (*33*), who demonstrated, in a major interlaboratory comparison, that the absolute values obtained for trace elements in fly ash varied considerably between techniques and between laboratories. Nevertheless, the reproducibilities obtained for a given element using a single technique were within 10% except for occasional samples where the deviations are attributed to poor sampling statistics as discussed earlier. Since our findings and conclusions rely only on the *relative* accuracies of values obtained for different size fractions using a single technique for each element, the uncertainties in absolute accuracy are not of major consequence in this work.

Acknowledgments

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Literature Cited

(1) Schroeder, H. A., *Environment*, 13, 18–32 (1971).
(2) Gordon, G. E., Zoller, W. H., "Normalizations and Interpretation of Atmospheric Trace-Element Concentration Patterns," Oak Ridge Trace Elements Conference, Oak Ridge, 1973.
(3) Morrow, P. E., *Amer. Ind. Hyg. Assoc. J.*, 25, 213–36 (1964).
(4) Hatch, T. F., Gross, Paul, "Pulmonary Deposition and Retention of Inhaled Aerosols," Academic Press, New York, N.Y., 1964.
(5) United States Department of Health, Education, and Welfare, National Air Pollution Control Boards, Pub. No. AP-49, "Air Quality Criteria for Particulate Matter," Washington, D.C., January 1969.
(6) Langham, W. W., "Radioisotope Absorption and Methods of Elimination: Relative Significance of Portals of Entry," in "Symposium on Radioisotopes in the Biosphere," R. S. Caldecott and L. A. Snyder, Eds., Minneapolis, University of Minnesota Press, 1960.
(7) Patterson, C. C., *Sci. Cit.*, 10, 66 (1968).
(8) Dautreband, L., "Microaerosols," Academic Press, New York, N.Y., 1962.
(9) Rahn, K. A., Dams, R., Robbins, J. A., Winchester, J. W., *Atmos. Environ.*, 5, 413 (1971).
(10) Lee, R. E., Jr., Goransen, S. S., Enrione, R. E., Morgan, G. B., *Environ. Sci. Technol.*, 6, 1025–30 (1972).
(11) Colovos, G., Wilson, G. S., Moyers, J. L., to be published in *Int. J. Environ. Anal. Chem.*, in press.
(12) Gladney, E. S., Zoller, W. H., Jones, A. G., Gordon, G. E., *Environ. Sci. Technol.*, 8, 551–7 (1974).
(13) Ranz, W. E., Wong, J. B., *Ind. Hyg. Occupa. Med.*, 4, 464–77 (1952).
(14) Flesch, J. P., Norris, C. H., Nugent, A. E., Jr., *Am. Ind. Hyg. Ass. J.*, 28, 507–16 (1967).
(15) Schmidt, F. J., Royer, J. L., *Anal. Lett.*, 6 (1), 17–23 (1973).
(16) Price, N. B., Angell, G. R., *Anal. Chem.*, 40 (3), 660–3 (1968).
(17) Farrar, Harry, IV, in "Trace Analysis by Mass Spectrometry," Arthur J. Ahearn, Ed., Chap. 8, Academic Press, New York, N.Y., 1972.
(18) Owens, E. B., Giardino, N. A., *Anal. Chem.*, 35, 1172 (1963).
(19) Steyermark, Al., "Quantitative Organic Microanalysis," p 222, Academic Press, New York, N.Y., 1961.

(20) Gordon, G. E., Director, "Study of the Emissions from Major Air Pollution Sources and Their Atmospheric Interactions, First Year Progress Report," Nov. 1, 1972-Oct. 31, 1973, University of Maryland, College Park, Md.
(21) Lee, R. E., Jr., von Lehmden, D. J., *J. Air Pollut. Contr. Ass.*, 23 (10), 853 (1973).
(22) Toca, F. M., "Lead and Cadmium Distribution in the Particulate Effluent from a Coal Fired Boiler," Ph.D. Dissertation, U. of Iowa, July 1972; see also *Diss. Abstr. Int.*, 33, 3156B (1973).
(23) Sparks, C. J., Oak Ridge National Laboratory, "Analysis of Particles Collected on a Brinks Impactor," private communication, 1973.
(24) Nicholls, G. D., in "Coal and Coal Bearing Strata," D. Merchison and P. Stanley Westoll, Eds., pp 269-307, Oliver and Boyd, London, 1968.
(25) Gluskoter, H. J., Lindahl, P. C., *Science*, 181, 264-6 (1973).
(26) Hulett, L. D., Oak Ridge National Laboratory, "Analysis of Individual Fly Ash Particles," personal communication, 1973.
(27) Hulett, L. D., *ibid.*, "The Chemical State of Sulfur in Fly Ash," personal communication, 1973.
(28) Butcher, S. S., Charlson, R. J., "An Introduction to Air Chemistry," Chap. 9, Academic Press, New York, N.Y., 1972.
(29) Gladney, E. S., Gordon, G. E., Zoller, W. H., "Abnormally Enriched Trace Elements in the Atmosphere," Seventh Annual Conference on Trace Substances in Environmental Health, U. of Missouri, Columbia, Mo., June 1973.
(30) Hodgeman, C. D., Ed.-in-chief, "Handbook of Chemistry and Physics," p 2429, 44th ed., The Chemical Rubber Publishing Co., Cleveland, Ohio, 1963.
(31) Pillay, K. K. S., Thomas, C. C., Jr., *J. Radioanal. Chem.*, 7, 107-18 (1971).
(32) Muller, R. O., "Spectrochemical Analysis of X-ray Fluorescence," pp 72-86, Plenum Press, New York, N.Y., 1972.
(33) von Lehmden, D. J., Jungers, R. H., Lee, R. E., Jr., *Anal. Chem.*, 46 (2), 239 (1974).

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Partition Coefficient to Measure Bioconcentration Potential of Organic Chemicals in Fish

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■ The bioconcentration of several chemicals in trout muscle was found to follow a straight line relationship with partition coefficient. Bioconcentration in this paper is defined as the ratio of the concentration of the chemical between trout muscle and the exposure water measured at equilibrium. Partition coefficient has the usual meaning in that it is the ratio of the equilibrium concentration of the chemical between a nonpolar and polar solvent (in this case, *n*-octanol and water were the two solvents used). The relationship was established by measuring the bioconcentration in trout of a variety of chemicals over a wide range of partition coefficients. An equation of the straight line of best fit was determined and used to predict the bioconcentration of other chemicals from their partition coefficients. The predicted values agreed with the experimental values in the literature.

The ability of some chemicals to move through the food chain resulting in higher and higher concentrations at each trophic level has been termed biomagnification or bioconcentration (*1*). The widespread distributions of DDT (*2*, *3*) and the polychlorinated biphenyls (PCBs) (*4*) have become classic examples of such movement. From an environmental point of view this phenomenon becomes important when the acute toxicity of the agent is low and the physiological effects go unnoticed until the chronic effects become evident. Due to the insidious nature of the bioconcentration effect, by the time chronic effects are noted, corrective action such as terminating the addition of the chemical to the ecosystem, may not take hold soon enough to alleviate the situation before irreparable damage has been done. For this reason prior knowledge of the bioconcentration potential of new or existing chemicals is desired. The importance of bioconcentration is also recognized by the Environmental Protection Agency (EPA). For example, the ability of a material to build up in the environment has become one of the proposed criteria that this regulatory agency is using in establishing toxic pollutant effluent standards (*5*).

In spite of the complexity of the reactions involved in the biomagnification process, we felt it important to see if a simple relationship could be established between the physicochemical properties of a chemical and its ability to bioconcentrate. It was our belief that the partition coefficient would be the most logical parameter to examine in this connection. If a simple relationship could be established it would be of great benefit in planning the future direction of any development work on a new chemical and in directing research efforts to determine the ultimate fate and distribution of others.

Materials and Methods

Chemicals. The following chemicals, representing a wide range of partition coefficients, were evaluated: 1,1,2,2-tetrachloroethylene, hexachlorobenzene, 2,2′,4,4′-tetrachlorobiphenyl, 2-biphenylyl phenyl ether, diphenyl ether, carbon tetrachloride, and *p*-dichlorobenzene. All materials were examined for purity by means of gas chromatography and found to be >99% pure.

Bioconcentration Factor in Fish. The method described by Branson et al. (*6*) was used to determine the bioconcentration factor in rainbow trout (*Salmo gairdneri* Richardson). This method is based on determining the ratio of the concentration of the chemical in trout muscle

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COMPOSITION AND SIZE DISTRIBUTION OF IN-STACK PARTICULATE MATERIAL AT A COAL-FIRED POWER PLANT

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Abstract—The particulate material in the stack effluent of a coal-fired power plant was collected and fractionated with an in-stack cascade impactor. Samples of the pulverized coal and process ashes were taken on the same days. These materials were analyzed for 34 elements by instrumental neutron and photon activation analysis. Elements on the in-stack particulates can be separated into three groups by computing enrichment factors relative to the coal for each particle size fraction. These groups are compared to proposed mechanisms for trace element fractionation during combustion.

With the increasing importance of coal as a fuel for electric power generation, there is renewed concern about the atmospheric emissions associated with coal combustion. Potentially toxic trace elements in the coal (e.g. Se, As, Hg, Pb, Sb, and Zn) may be volatilized at the temperatures encountered in the combustion zone and either redistributed onto the smaller particles entrained in the flue gas or emitted in the gas phase. The enrichment of certain trace elements on smaller particles has been discussed by Billings and Matson (1972), Billings *et al.* (1973), Gordon *et al.* (1973), Gladney *et al.* (1974), Natusch and Wallace (1974), Natusch *et al.* (1974), Kaakinen *et al.* (1975), Klein *et al.* (1975), Lee *et al.* (1975) and Ragaini and Ondov (1975). Since coal-fired generating stations are a large source of particulate material, the emission of substantial fractions of toxic trace elements on respirable particles could pose a distinct health hazard. It is important, therefore, to measure both the composition and the particle size distribution of the emitted material.

Urban particulates of dia. $\leq 1.0\ \mu m$ have unusually high enrichments of some 15 trace elements (Lee *et al.*, 1972; Gordon *et al.*, 1973; Gladney *et al.*, 1974). Sources for a few of these elements have been traced to auto emissions (Moyers *et al.*, 1972) and residual-oil combustion (Zoller *et al.*, 1973); however, sources for many of these elements remain to be identified. Careful characterization of coal-fired plant emissions should establish the importance of this source in the complex of urban emissions. Size distribution measurements may also permit the differentiation of coal-fired particulates from those of continental origin, and permit the evaluation of the former's contribution to both major- and trace-element levels observed on urban air particulates.

EXPERIMENTAL

Several varieties of cascade impactors are available for in-stack particulate sampling. The University of Washington Mark III Cascade Impactor (Pilat *et al.*, 1970) was selected as the instrument best designed to minimize wall-loss and reentrainment of collected particulates as well as having the lowest 50% effective cutoff diameter (ECD) on the final stage. This instrument can be readily attached ahead of a modified EPA sampling train (Rom, 1972; Gladney, 1974) and operated under EPA-sanctioned sampling conditions.

Impactor, pulverized coal and process ash samples were taken on several different days at the Potomac Electric Power Company's (PEPCO) Chalk Point Electric Generating Station in rural south-eastern MD. At the time of sampling the plant consisted of two 355 MW(e) generators, each consuming 10^5 kg of coal h^{-1} at full load (Berberich and Baver, 1964). The coal is ground to 50 mesh and blown from pulverizer into the furnace (water wall), and ash and flue gases are blown from the furnace through the economizer, past Cottrell electrostatic precipitators, and out two 120 m stacks. A small fraction of the coal ash (approx. 9%) is retained in the furnace and removed as bottom slag. About 12% of the ash, predominately particles of 0.1–2 mm dia., is collected at the economizer and about 75% of the ash is trapped by the precipitators and deposited in the fly ash hoppers (Reese, 1974). Approximately 4% of the total ash remains entrained in the flue gas and is emitted to the atmosphere (Whang, 1974).

The temperature of the flue gas is monitored at a number of points throughout the plant. The maximum temperature achieved in the combustion zone is 1600°C. The exhaust gas cools to 450°C during passage through the economizer. The temperatures of the inlet and outlet of the precipitator and at the base of the stack where the suspended particulates were sampled are 130, 120, and 110–120°C respectively (Reese, 1974).

The first seven stages of the Mark III impactor were covered with thin polycarbonate films that had been coated on one side with a thin layer of silicone resin. This sticky surface was employed in an effort to minimize particle bounce-off. Several different filter materials were investigated for use on the final stage of the impactor (an

Table 1. Effective cut-off diameters of mark III source test cascade impactor

Stage	ECD (μm)
1	30
2	14
3	6.0
4	2.5
5	1.4
6	0.70
7	0.35

in-line filter). Nuclepore polycarbonate filters (0.45 μm pore dia.) were selected as the best compromise among filtering capacity, blank levels, and heat resistance. This impactor has 50% ECD's shown in Table 1 when operated at a flow rate of 19.8 min^{-1} and at 130 C (Pilat *et al.*, 1973).

Ten minute isokinetic cascade impactor samples were taken using a modified EPA sampling train (details in Martin, 1971; Rom, 1972; Gladney, 1974). A 10 cm plug was designed so that an S-type Pitot tube, a pyrometer, and the impactor could be inserted in the port at the base of the stack simultaneously. The impactor would have its opening pointing "downstream" so that it could be warmed to stack temperature before sampling to avoid condensing volatiles from the gas stream during sampling. During this preheating process, the temperature and velocity of the stack gases were measured with the pyrometer and Pitot tube. These values were monitored for about 10 min, and if conditions were stable a sample was taken.

ANALYSIS

All samples were analyzed nondestructively by instrumental neutron and photon activation analyses. The analytical techniques, described in detail by Gladney (1974), were modified versions of those reported by Zoller and Gordon (1970) and Aras *et al.* (1973) for all elements except Hg. This element was measured by a combustion procedure described by Rook *et al.* (1972) on only a single impactor run. The powdered coal and fly ash were encapsulated in precleaned polyethylene vials and each impactor stage was folded and individually packaged in clean polyethylene bags. These samples were irradiated simultaneously with National Bureau of Standards (NBS) Standard Reference Materials (SRM) No. 1632 (coal) and No. 1633 (fly ash) and a solid multi-element standard prepared by pipetting a mixed elemental solution onto Whatman No. 1 filter paper. Neutron irradiations were performed at the NBS reactor at a flux of 6×10^{13} n cm^{-2} sec^{-1}, and photon irradiations were carried out at the NBS electron linac.

Spectra of the γ-rays emitted by the samples were observed several times after the various irradiations with large, high resolution Ge(Li) detectors (full-width at half maximum of 1.8 at 1332 keV) coupled to 4096-channel pulse-height analyzers. The spectra were stored on magnetic tape and the data reduced off-line by computer. Quality control of these analyses was assured by analysis of the NBS SRM's (reported in Gladney, 1974). The results for all elements compared well with data reported by Ondov *et al.* (1975) and with the NBS certified values (NBS, 1974). The uncertainties on all elemental concentration data reported in this paper are ±10%.

RESULTS AND DISCUSSION

Elemental concentrations in the coal, precipitator fly ash, and the suspended particulates are given in Table 2 for selected elements. Runs 1–3 were similar in nature and have been averaged, while individual

Table 2. Elemental concentrations in power plant materials

Element	Run	Coal (ppm)	Precip. Fly Ash (ppm)	Impactor stage (μg m^{-3}) 1	2	3	4	5	6	7	Filter	TSP*
Al	1–3	17600	130000	2300	810	1500	2300	1700	450	210	380	9600
	4	18800	135000	24	79	600	1040	810	440	52	580	3600
Na	1–3	258	2090	36	12	25	33	25	7.2	3.3	6.2	148
	4	287	2370	0.43	1.4	11	18	14	7.7	0.91	10	64
Br	1–3	42.3	6.36	0.14	0.22	0.26	0.20	0.17	0.13	0.15	0.79	2.1
	4	38.2	6.21	0.041	0.058	0.054	0.049	0.039	0.034	0.040	2.3	2.6
I	1–3	48.4	96.9	8.1	2.2	1.9	1.7	1.2	0.91	0.93	10	27
	4	52.8	131	0.72	1.1	1.3	2.2	2.6	2.7	0.36	19	30
Cr	1–3	26.3	180	3.2	1.1	2.2	3.4	2.2	0.64	0.38	1.6	15
	4	28.4	192	0.032	0.21	0.80	1.9	1.6	0.79	0.20	1.8	7.3
Ni	1–3	22.3	151	4.8	1.4	2.3	3.8	2.7	0.77	0.45	1.8	18
	4	22.0	143	0.16	0.30	1.1	2.6	1.3	0.83	0.065	1.4	7.8
Zn	1–3	27.9	229	4.7	1.8	4.0	5.1	3.8	1.0	0.63	1.3	22
	4	28.4	259	0.065	0.17	1.4	1.9	1.6	1.0	0.13	2.4	8.6
Ga	1–3	11.1	92.5	0.65	0.52	1.2	1.8	1.2	0.57	0.23	0.64	6.8
	4	13.9	81.8	0.024	0.062	0.46	0.88	0.84	0.50	0.044	0.86	3.7
As	1–3	26.0	168	6.0	3.5	8.3	12	11	5.3	3.1	32	81
	4	24.3	124	0.45	1.6	3.0	5.0	5.0	3.5	1.3	28	48
Se	1–3	3.96	23.8	3.1	3.3	3.1	1.9	0.72	0.33	0.22	1.1	14
	4	6.42	26.6	0.050	0.42	2.6	0.93	0.38	0.20	0.16	1.9	6.6
Sb	1–3	0.812	5.61	0.083	0.13	0.21	0.35	0.25	0.090	0.068	0.59	1.8
	4	1.06	7.68	0.010	0.024	0.074	0.17	0.17	0.12	0.047	0.71	1.3
Pb	1–3	10.2	59.6	1.3	1.0	2.6	2.9	2.2	0.89	0.48	3.6	15
	4	6.47	66.4	0.030	0.12	0.68	1.8	2.3	1.1	0.58	3.9	10
Hg	2	0.36	0.075	0.060	0.050	0.042	0.021	0.021	0.016	0.050	2.4	2.7

* Total suspended particulates (μg m^{-3}).

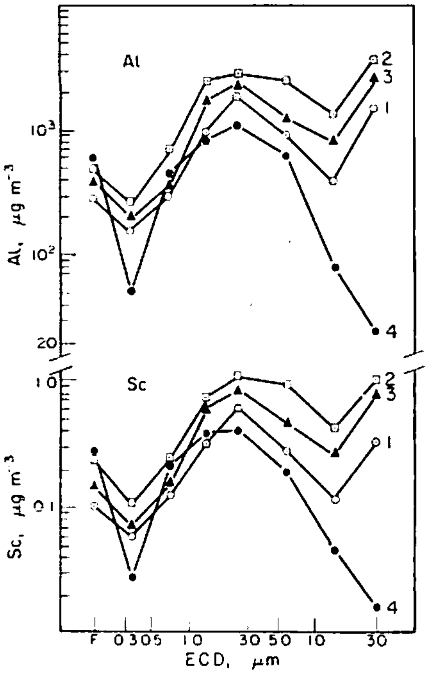

Fig. 1. In-stack size distribution of suspended particulates bearing Al and Sc at the Chalk Point Power Plant (F = backup filter)

data are presented for Run 4. Total suspended particulates are calculated by summing the concentrations across the eight impactor stages. Detailed tabular data for the 21 additional elements are reported in Gladney (1974).

Size distributions for Al, Sc, Br, and I are shown in Figs. 1 and 2. The size distributions for K, Rb, Mg, Ca, Sr, Ba, Zr, Th, Hf, Ta, V, Mn, Fe, Se, Sb, As, Ni, Cr, Co, Ti, Ga, Pb, Zn, Hg, Ce, La, Sm, Eu, Lu, and Yb were also measured, but are not shown.

The qualitative features shown by these figures are the same for all elements listed above except Hg and the halogens. Runs 1–3 usually show a higher trace element concentration on the first stage than on the second, since the particle fraction collected by the initial stage represents an integration over particle diameters greater than 30 μm. The fourth run was taken especially to get a lightly loaded sample and to avoid sampling particulates emitted as a result of "rapping" the precipitator. The rapping process removes particulates adhering to the high voltage wires in the Cottrell precipitator and results in a pulse of large diameter particulates being reentrained in the flue gas. The maximum elemental concentration occurs on particles of approx. 3 μm dia. for all four runs (except for Hg and halogens). In general, all curves, except those of Hg and the halogens, have similar shapes.

An enrichment factor, EF, for element X on each stage relative to average composition of Chalk Point Coal can be calculated using the following equation:

$$EF = ([X]_s/[\mathrm{Al}]_s)/([X]_c/[\mathrm{Al}]_c),$$

where $[X]_s$ and $[X]_c$ represent the concentrations of element X in the sample and the coal respectively, and $[\mathrm{Al}]_s$ and $[\mathrm{Al}]_c$ represent the concentrations of aluminium in the sample and the coal respectively (Gordon and Zoller, 1973). Average EF's, relative to Chalk Point coal, for the fly ash and suspended particulates for runs 1–3, and individual values for run 4, are shown in Table 3. Mercury was measured only on Run 2 and the EF's reported have been calculated using Hg and Al data for the coal and fly ash collected on that day only.

When the EF is plotted as a function of particle size, the trace elements can be broken into at least three groups. The Na distribution depicted in Fig. 3 is typical of the first group. This distribution is almost completely featureless— the particulates have the same ratio of Na/Al as the coal across the whole size spectrum. Several elements thought to be fairly volatile (and sometimes seen at high enrichments in ambient aerosols), such as Cr, Zn, Ni, and Ga also exhibit relatively little increase in EF relative to coal. Other elements that fall into this group, and whose EF distributions have also not been shown, are K, Rb, Mg, Ca, Sr, Ba, Sc, Ti, V, Mn, Co, Zr, Th, Hf, Ta, and all rare earths except Ce.

A second group of trace elements (Pb, As, and Sb) exhibits a definite increase in EF on smaller particles. The As EF distribution shown in Fig. 4 supports the hypothesis that these elements may be condensing out of the gas phase. The Sb and Pb distributions are similar and are not shown. It is difficult to compare these observations directly with those of Natusch *et al.* (1974) since no data on coal composition and only limited data on Al concentration as a function of particle size were reported. However, the concentration

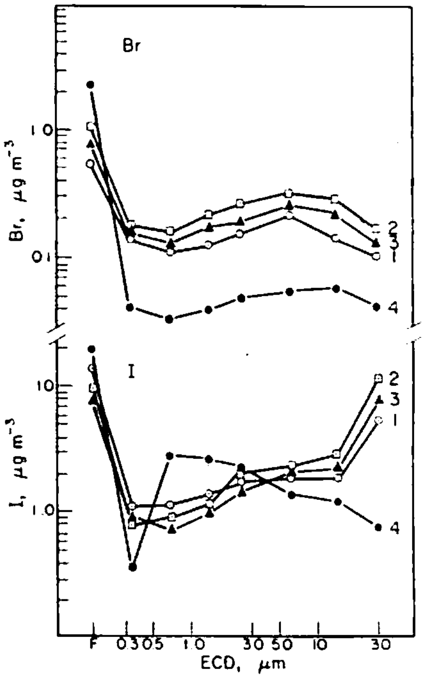

Fig. 2. In-stack size distributions of suspended particulates bearing Br and I at the Chalk Point Power Plant (F = backup filter).

Table 3. Enrichment factors of precipitator fly ash and suspended particulates relative to Chalk Point coal

		Precip	Impactor stage								
Element	Run	Fly Ash	1	2	3	4	5	6	7	Filter	TSP*
Na	1–3	1.1	1.1	1.0	1.1	0.98	1.0	1.1	1.1	1.1	1.0
	4	1.2	1.2	1.2	1.2	1.1	1.1	1.1	1.1	1.1	1.2
Br	1–3	0.020	0.025	0.11	0.18	0.036	0.087	0.12	0.30	0.86	0.091
	4	0.023	0.84	0.36	0.044	0.023	0.024	0.038	0.38	2.0	0.36
I	1–3	0.26	1.7	1.3	0.62	0.36	1.3	1.0	2.2	13	1.4
	4	0.34	11	5.0	0.77	0.75	1.1	2.2	2.5	12	3.0
Cr	1–3	0.93	0.93	0.91	0.98	0.99	0.87	0.95	1.2	2.8	1.0
	4	0.94	0.88	1.8	0.88	1.2	1.3	1.2	2.5	2.0	1.3
Ni	1–3	0.92	1.6	1.4	1.2	1.3	1.2	1.4	1.7	3.7	1.5
	4	0.90	5.7	3.2	1.6	2.1	1.4	1.6	1.1	2.1	1.8
Zn	1–3	1.1	1.3	1.4	1.7	1.4	1.4	1.4	1.9	2.2	1.5
	4	1.3	1.8	1.4	1.5	1.2	1.3	1.5	1.7	2.7	1.6
Ga	1–3	1.1	0.45	1.0	1.3	1.2	1.1	2.0	1.7	2.7	1.1
	4	0.82	1.4	1.1	1.0	1.1	1.4	1.5	1.1	2.0	1.4
As	1–3	0.88	1.8	2.9	3.7	3.5	4.4	7.8	10	57	5.7
	4	0.71	14	16	3.8	3.7	4.8	6.0	19	37	10
Se	1–3	0.81	6.0	18	9.2	3.7	1.9	3.2	4.6	13	6.5
	4	0.58	6.1	16	13	2.6	1.4	1.3	9.0	9.6	5.4
Sb	1–3	0.94	0.78	3.5	3.0	3.3	3.2	4.3	7.0	34	4.1
	4	1.0	7.4	5.4	2.2	2.9	3.7	4.8	16	22	6.4
Pb	1–3	0.79	0.98	2.1	3.0	2.2	2.2	3.4	3.9	16	2.7
	4	1.4	3.6	4.4	3.3	5.0	8.2	7.3	30	19	8.1
Hg	2	0.028	0.31	0.80	0.46	0.12	0.16	0.55	3.1	80	17

* Total suspended particulates.

enhancement of these elements on the smaller particles at Chalk Point is less marked than that reported by Natusch *et al.* (1974) for Illinois power plants.

Selenium, Hg, Br, and I also fall in this second group, but they are especially interesting since their EF distributions differ in important detail from the other three elements. Since I and Br are bimodal and similar to Se (Fig. 5), except that enrichment on the smaller particles is more pronounced, individual figures for these two elements are not presented. Selenium and Hg (Figs. 5 and 6), two of the most volatile elements studied, would be expected to epitomize the small particle preference resulting from condensation of these elements from the gas phase. As shown in Fig. 5, this is not completely true for Se. There is an enrichment of Se on smaller particles (although not to the same extent as Pb, As, and Sb), but there is also a substantial enrichment on the largest particles with a distinct minimum in the middle-sized particles (5.0 μm ≤ d ≤ 0.7 μm). Mercury also

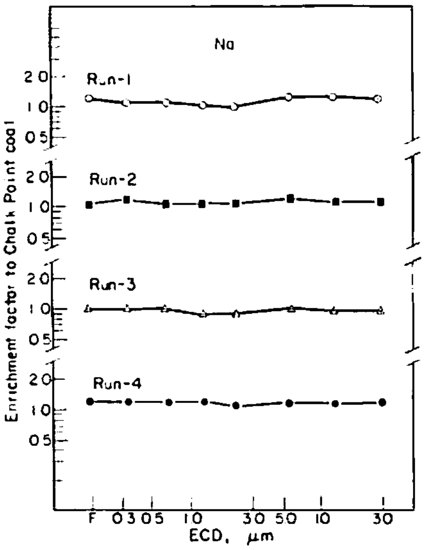

Fig. 3. Enrichment factor of Na, with respect to Chalk Point coal; as a function of in-stack particle size (F = backup filter).

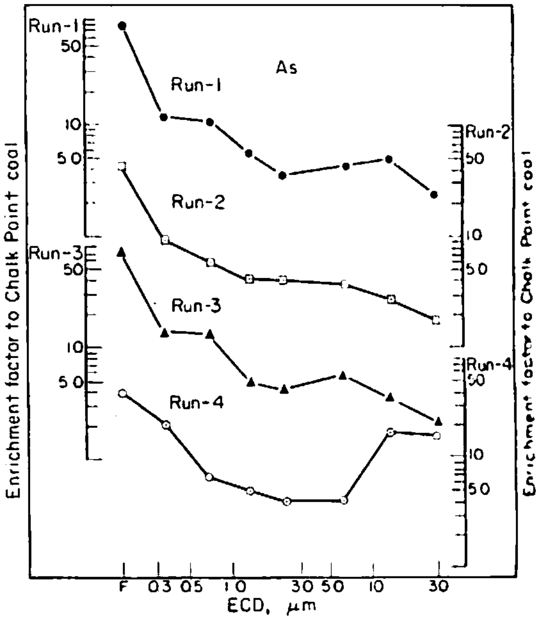

Fig. 4. Enrichment factor of As, with respect to Chalk Point coal, as a function of in-stack particle size (F = backup filter).

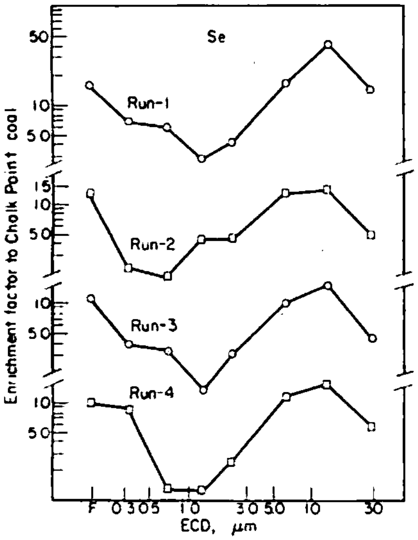

Fig. 5. Enrichment factor of Se, with respect to Chalk Point coal, as a function of in-stack particle size (F = backup filter).

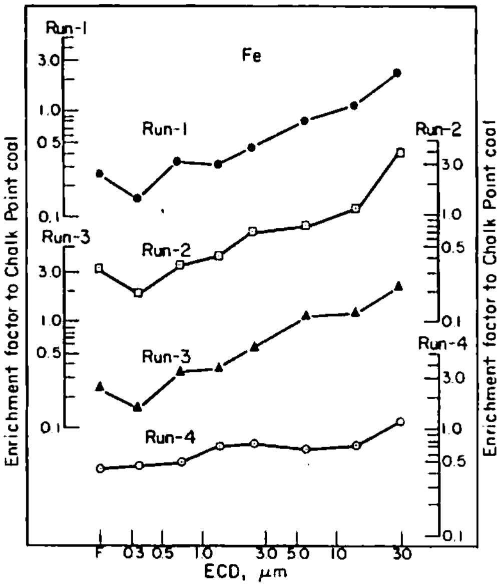

Fig. 7. Enrichment factor of Fe, with respect to Chalk Point coal, as a function of in-stack particle size (F = backup filter).

has an EF minimum in the mid-size range, but the enrichment on the smallest particles is very dramatic, which agrees with other power plant studies that focused on this element (Billings and Matson, 1972; Billings *et al.*, 1973). The model for gas phase condensation proposed by Natusch *et al.* (1974) does not adequately explain this bimodal behavior for Se, Br, I, and to a lesser extent Hg. It would be extremely useful to carefully characterize the gas phase concentrations of these elements inside the stack as an approach to explaining their peculiar distributions.

The final group of elements, consisting of Fe (Fig. 7) and Ce, exhibit a strong depletion with decreasing particle size. In the case of Fe, this might be explained by noting that most of the Fe in the coal is probably in a pyrite mineral phase (Ruch *et al.*, 1973). Since pyrites probably behave differently from aluminosilicates during combustion, Fe might be expected to yield a rather different size distribution. Other ash fractions retained inside the plant have higher EF's for Fe than the fly ash and suspended particulates, reinforcing the idea that Fe is concentrated on the larger particles (Gladney, 1974). At the present time it is not known if Fe and Ce are associated on the same particles so that the applicability of this hypothesis for Ce cannot be determined. Cerium does not follow the Fe enrichment pattern in bottom slag and economizer ash.

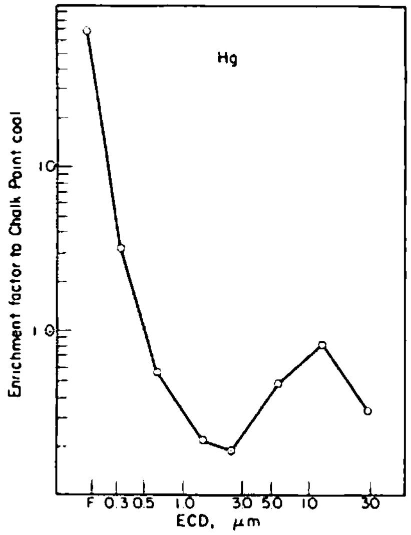

Fig. 6. Enrichment factor of Hg, with respect to Chalk Point coal, as a function of in-stack particle size (F = backup filter), Run 2 only.

Two other power plant studies (Kaakinen *et al.*, 1975; Ragaini and Ondov, 1975) present sufficient data from in-stack elemental measurements to permit a comparison. Average *EF*'s for seven elements have been calculated relative to the coal burned from these two studies and are shown in Table 4. The agreement among these three in-stack sampling efforts is reason-

Table 4. Comparison of enrichment factors for in-stack total suspended particulates*

Element	Present work†	Kaakinen *et al.*‡	Ragaini & Ondov§
Aa	6.8	3.1	7.3 ± 3.2
Zn	1.5	3.2	6.4 ± 4.4
Sb	4.7	3.2	6.7 ± 1.6
Se	6.2	5.7	2.5 ± 1.1
Pb	4.0	5.8	—
Ga	1.2	--	3.1 ± 0.7
Cr	1.1	--	2.0 ± 0.3

* All EF's are relative to coal burned.
† Weighted average from Table 3.
‡ Precipitator outlet stream.
§ Mean ± standard deviation for unspecified number of samples.

ably good, considering differences in sampling conditions, and power plant design and operating parameters. Zinc is definitely less enriched in the Chalk Point stack emissions, although the uncertainties in Ragaini and Ondov (1975) are high. Gallium also appears to be significantly less enriched at Chalk Point. These differences may be attributable to lower combustion and in-stack temperatures at Chalk Point. The behavior of the other elements seems to be relatively similar at the three power plants.

SUMMARY AND CONCLUSIONS

The University of Washington Mark III Cascade Impactor used in this work provided good separation of particles of different sizes as shown by the contrast in size distribution curves for different elements and by comparison with trace element size distributions from other sources (Greenberg, 1974).

Three broad classes of enrichment factor distributions for particulates have been identified. Most elements show little, if any, enrichment (compared to the input coal) as a function of particle size (e.g. Fig. 3); several of the more volatile, toxic trace elements (Sb, As, Pb, Hg, Se, Br, and I) do exhibit increased enrichments on the smaller particles; and two elements, Fe and Ce, had decreasing enrichment with decreasing particle size.

The trace elemental concentration patterns and enrichment factors as functions of particle size suggest that coal-fired power plants similar to Chalk Point, despite the emission of tons of particulate matter, do not seem to account for the high enrichment factors observed for certain particulate trace elements in cities. The nature of the trace metal emissions may be strongly influenced by the temperatures within the plant and the precipitator efficiencies at different facilities. This aspect has been discussed elsewhere (Zoller *et al.*, 1974). A number of other plants should be studied to elucidate the impact of operating conditions on the particle size distribution of the toxic trace elements. Furthermore, the gas phase components of the trace elements requires investigation.

These in-stack elemental distributions do not match the ambient particle size distributions observed for many trace elements in urban areas. Elements which are highly enriched on city aerosols (e.g. V, Zn, Se and Sb) exhibit a strong increase in concentration with decreasing particle size, with typically 50% of their elemental mass found on particles of $d \leq 1.0\,\mu$m and *EF*'s greater than 1000 (Gladney *et al.*, 1974). The in-stack concentration distributions for all elements show distinct minima in the region $0.3 \leq d \leq 1.0\,\mu$m and EF's of less than 100 on the smallest particles. If the differences between these distributions are observed at most coal-fired power stations, this suggests that the emissions from coal-fired installations do not have a major impact on the observed urban particle size distributions (Lee *et al.*, 1968; Nifong and Winchester, 1970; Lee *et al.*, 1972; Gladney *et al.*, 1974) for many toxic trace elements.

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REFERENCES

Aras N. K., Zoller W. H., Gordon G. E. and Lutz G. J. (1973) Instrumental photon activation analysis of atmospheric particulate material. *Analyt. Chem.* 45, 1481–1490.

Berberich C. E. and Baver C. B. (1964) Design features of the Chalk Point Generating Station. Presented at Southeastern Electric Exchange, Washington, D.C.

Billings C. E. and Matson W. R. (1972) Mercury emissions from coal combustion. *Science* 176, 1232–1233.

Billings C. E., Sacco A. M., Matson W. R., Griffin R. M., Coniglio W. R. and Harley R. A. (1973) Mercury balance on a large pulverized coal-fired furnace. *J. Air Pollut. Control Ass.* 23, 773–777.

Gladney E. S. (1974) Trace element emissions from coal-fired power plants: A study of the Chalk Point Electric Generating Station. Ph.D. Thesis, University of Maryland.

Gladney E. S., Zoller W. H., Jones A. G. and Gordon G. E. (1974) Composition and size distribution of atmospheric particulate matter in the Boston area. *Environ. Sci. Technol.* 8, 551–557.

Gordon G. E., Zoller W. H. and Gladney E. S. (1973) Abnormally enriched trace elements in the atmosphere. *Trace Substances in Environmental Health VII* (Edited by Hemphill D. D.), pp. 167–174. University of Missouri, Columbia, MO.

Gordon G. E. and Zoller W. H. (1973) Normalization and interpretation of atmospheric trace element concentration patterns. *Proc. 1st Annual NSF Trace Contaminants Conference*, Oak Ridge National Laboratory, Oak Ridge, Tenn., CONF-730802 pp. 314–325.

Greenberg R. R. (1974) University of Maryland, private communication.

Kaakinen J. W., Jorden R. M., Lawasani M. H. and West R. E. (1975) Trace element behavior in coal-fired power plant. *Environ. Sci. Technol.* 9, 862–869.

Klein D. H., Andren A. W., Carter J. A., Emery J. F., Feldman C., Fulkerson W., Lyon W. S., Ogle J. C., Talmi Y., Van Hook R. I. and Boulton N. (1975) Pathways of thirty-seven elements through coal-fired power plant. *Environ. Sci. Technol.* 9, 973–979.

Lee R. E., Patterson R. K. and Wagman J. (1968) Particle size distribution of metal components in Urban air. *Environ. Sci. Technol.* 2, 288–290.

Lee R. E., Goranson S., Enrione R. and Morgan G. (1972) The NASN cascade impactor network—II. Size distributions of trace metal components. *Environ. Sci. Technol.* 6, 1025–1030.

Lee R. E., Crist, H. L., Riley A. E. and MacLeod K. E. (1975) Concentration and size of trace metal emissions from a power plant, a steel plant, and a cotton gin. *Environ. Sci. Techol.* 9, 643–647.

Martin R. M. (1971) Construction details of isokinetic source-sampling equipment. Air Pollution Control Office, EPA, Research Triangle Park, N.C., Pub. No. APTD-0581.

Moyers J. L., Zoller W. H., Duce R. A. and Hoffman G. L. (1972) Gaseous bromine and particulate lead, vanadium and bromine in a polluted atmosphere. *Environ. Sci. Technol.* 6, 68–71.

National Bureau of Standards (1974) Certificate of Analysis, Standard Reference Material No. 1632 (Coal), Washington, D.C.

National Bureau of Standards (1974) Certificate of Analysis, Standard Reference Material No. 1633 (Coal Fly Ash), Washington, D.C.

Natusch D. F. S., Wallace J. R. and Evans C. A. (1974) Toxic trace elements: preferential concentration in respirable particles. *Science* 183, 202–204.

Natusch D. F. S. and Wallace J. R. (1974) Urban aerosol toxicity: the influence of particle size. *Science* 186, 695–699.

Nifong G. D. and Winchester J. W. (1970) Particle size distributions of trace elements in polluted aerosols. University of Michigan, Report C001705B.

Ondov J. M., Zoller W. H., Olmez I., Aras N. K., Gordon G. E., Rancitelli L. A., Abel K. H., Filby R. H., Shag K. R. and Ragaini R. C. (1975) Elemental concentrations in the NBS environmental coal and fly ash standard reference materials. *Analyt. Chem.* 47, 1102–1109.

Pilat M. J., Ensor D. S. and Bosch J. C. (1970) Source test cascade impactor. *Atmospheric Environment* 4, 671–679.

Pilat M. J., Ensor D. S. and Shattenburg G. E. (1973) *Operation Manual for Mark III University of Washington Source Test Cascade Impactor.*

Ragaini R. C. and Ondov J. M. (1975) Trace contaminants from coal-fired power plants. International Conference on Environmental Sensing and Assessment, Las Vegas, NV.

Reese C. (1974) Plant Manager, Chalk Point, Potomac Electric Power Co., private communication.

Rom J. J. (1972) Maintenance, calibration, and operation of isokinetic source-sampling equipment. Office of Air Programs, EPA, Research Triangle Park, N.C., Pub. No. APTD-0576.

Rook H. L., Gills T. E. and LaFleur P. D. (1972) Method for determination of mercury in biological materials by neutron activation analysis. *Analyt. Chem.* 44, 1114–1117.

Ruch R. R., Gluskoter H. J. and Shimp H. F. (1973) Occurrence and distribution potentially volatile trace elements in coal: An interim report. Environmental Geology Notes Vol. 61. Illinois Geological Survey, Urbana, IL.

Whang J. S. (1974) Real-time characterization of particulates emitted by a coal-fired power plant. Ph.D. Thesis, University of Maryland.

Zoller E. H. and Gordon G. E. (1970) Instrumental neutron activation analysis of atmospheric pollutants utilizing Ge(Li) gamma-ray detectors. *Analyt. Chem.* 42, 257–265.

Zoller W. H., Gordon G. E., Gladney E. S. and Jones A. G. (1973) The sources and distribution of vanadium in the atmosphere. In *Geochemical Cycles of Trace Elements in Our Environment* (Edited by Kothny E. L.), *Advances in Chemistry Series* pp. 31–47. No. 123. American Chemical Society, Washington, D.C.

Zoller W. H., Gladney E. S., Gordon G. E. and Bors J. J. (1974) Emissions of trace elements from coal-fired power plants. In *Trace Substances in Environmental Health VIII* (Edited by Hemphill D. D.). Vol. 8, pp. 167–172. University of Missouri, Columbia, MO.

Eng., 90, 79–107 (1964).
(27) Adamson, A. W., "Physical Chemistry of Surfaces", 2nd ed., Interscience, New York, 1967, p 573.
(28) Lemieux, R., Morrison, J., *Can. J. Res.*, 25B, 212 (1947).
(29) Zechmeister, L., "Progress in Chromatography", Wiley, New York, 1950, p 189.
(30) Weber, W. J., Jr., van Vliet, B. M., presented at the 176th National Meeting of the American Chemical Society, Miami, Fla., Sept 10–15, 1978.
(31) Liapis, A. I., Rippin, D. W. T., *Chem. Eng. Sci.*, 32, 619 (1977).
(32) Butler, J. A. V., Ockrent, C. J., *J. Phys. Chem.*, 34, 2841 (1930).
(33) Jain, J. S., Snoeyink, V. L., *J. Water Pollut. Control Fed.*, 45, 2463–79 (1973).
(34) Radke, C. J., Prausnitz, J. M., *AIChE J.*, 18, 761–8 (1972).
(35) Jossens, L., Prausnitz, J. M., Fritz, W., Schunder, E. U., Myers, A. L., *Chem. Eng. Sci.*, 33, 1097 (1978).
(36) Myers, A. L., Prausnitz, J. M., *AIChE J.*, 11, 121 (1965).
(37) DiGiano, F. A., Baldauf, G., Frick, B., Sontheimer, H., *Chem. Eng. Sci.*, 33, 1667–73 (1978).
(38) Manes, M., presented at the 176th National Meeting of the American Chemical Society, Miami, Fla., Sept 10–15, 1978.
(39) Hofer, L. J. E., Manes, M., *Chem. Eng. Prog.*, 65, 84 (1969).
(40) Manes, M., Hofer, L. J. E., *J. Phys. Chem.*, 73, 584 (1969).
(41) Wohleber, D. A., Manes, M., *J. Phys. Chem.*, 75, 61 (1971).
(42) Wohleber, D. A., Manes, M., *J. Phys. Chem.*, 75, 3720 (1971).
(43) Rosene, M. R., Ozcan, M., Manes, M., *J. Phys. Chem.*, 80, 2586 (1976).
(44) McGuire, M. J., Suffet, I. H., Radzail, J. V., *J. Am. Water Works Assoc.*, 70, 565 (Oct 1978).
(45) McGuire, M. J., Ph.D. Thesis, Drexel University, Philadelphia, 1977.
(46) Keller, R. A., Snyder, L. R., *J. Chromatog. Sci.*, 9, 346 (1971).
(47) Sinanoglu, O., in "Molecular Associations XIN Biology", Pullman, B., Ed., Academic Press, New York, 1968, pp 427–45.
(48) Sinanoglu, O., Abdulnur, S., *Fed. Proc., Fed. Am. Soc. Exp. Biol.*, 24, No. 2, Part III, S-12 (1965).
(49) Halicioglu, T., Sinanoglu, O., *Ann. N.Y. Acad. Sci.*, 158, 308 (1969).
(50) Horvath, C., Melander, W., Molnar, I., *J. Chromatogr.*, 125, 129 (1976).
(51) Aberhalden, E., Foder, A., *Fermentforschung*, 2, 74, 151 (1910).
(52) Cheldin, V. H., Williams, R. J., *J. Am. Chem. Soc.*, 64, 1513 (1942).
(53) Tiselius, A., Ed., The Svedberg, Almquist and Wiksells, Upsala, 1944, p 370.
(54) Williams, R. J. P., Hagdahl, L., Tiselius, A., *Ark. Kemi*, 7, 1 (1954).
(55) Colin, H., Eon, C., Guiochon, G., *J. Chromatogr.*, 119, 41 (1970).
(56) Colin, H., Eon, C., Guiochon, G., *J. Chromatogr.*, 122, 223 (1976).
(57) Colin, H., Guiochon, G., *J. Chromatogr.*, 137, 19 (1977).
(58) Colin, H., Ward, N., Guiochon, G., *J. Chromatogr.*, 149, 169 (1978).
(59) Colin, H., Guiochon, G., *J. Chromatogr.*, 158, 183 (1978).
(60) Horvath, C., Melander, W., Molnar, I., *Anal. Chem.*, 49, 142 (1977).
(61) Horvath, C., Melander, W., *Am. Lab.*, 10, 17 (1978).
(62) Franks, H. S., Evans, M. W., *J. Chem. Phys.*, 13(11), 507 (1945).
(63) Kauzmann, W., *Adv. Protein Chem.*, 14, 1 (1959).
(64) Tanford, C., *Science*, 200, 1012 (1978).
(65) Sourirajan, S., Matsuura, T., "Reverse Osmosis and Synthetic Membranes", Sourirajan, S., Ed., National Research Council Canada, Ottawa, Canada, 1977, pp 5–43.
(66) Barrow, G. M., *J. Phys. Chem.*, 59, 1129 (1955).
(67) Gordy, W., *J. Chem. Phys.*, 7, 93–9 (1939).
(68) Gordy, W., Stanford, S. C., *J. Chem. Phys.*, 8, 170–7 (1940).
(69) Gordy, W., Stanford, S. C., *J. Chem. Phys.*, 9, 204–14 (1941).
(70) Gordy, W., *J. Chem. Phys.*, 9, 215–23 (1941).
(71) Kuhn, L. P., *J. Am. Chem. Soc.*, 74, 2492–9 (1952).
(72) Kagija, T., Sumida, Y., Inoue, T., *Bull. Chem. Soc. Jpn.*, 41, 767 (1968).
(73) Taft, R. W., Jr., in "Steric Effects in Organic Chemistry", Newman, M. S., Ed., Wiley, New York, 1956, pp 556–675.
(74) Hammett, L. P., "Physical Organic Chemistry", 2nd ed., McGraw-Hill, New York, 1970, pp 347–90.
(75) Pinsky, J., *Mod. Plast.*, 34(4), 145 (1957).
(76) Diamond, J. M., Wright, E. M., *Annu. Rev. Physiol.*, 31, 581–646 (1969).

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Emissions and Particle-Size Distributions of Minor and Trace Elements at Two Western Coal-Fired Power Plants Equipped with Cold-Side Electrostatic Precipitators

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■ Concentrations and distributions according to particle size of up to 42 elements were measured in aerosol particles collected in-stack at two western coal-fired power plants equipped with cold-side electrostatic precipitators (ESP). Elements were measured by instrumental neutron activation analysis, atomic absorption spectroscopy, and X-ray fluorescence. Particle-size distributions in filter and cascade impactor samples from both units were bimodal. Most of the particulate material from the units was emitted as large particles with mass median aerodynamic diameters of >1.6 μm. Emission rates normalized per joule of input heat strongly reflect differences in the type and efficiency of the control devices and the chemistry of the coal. However, the relative penetrations of many elements at both plants were remarkably similar despite major differences in coal composition and plant design. Our results are compared with those of three other studies of similarly equipped power plants. Relative penetrations of Zn, Pb, Ba, Cr, Co, V, Rb, and Sb differed significantly among the five plants.

The National Coal Association forecasts an increase in utility coal usage from 4.0×10^{11} kg in 1976 to approximately 7.7×10^{11} kg in 1985. The nation's expanding reliance on coal combustion in the production of electric power has increased the importance of evaluating the associated potential biomedical and environmental hazards. Coal combustion results in the release into the atmosphere of a number of potentially toxic substances, including naturally occurring radionuclides (*1–5*), polynuclear aromatic hydrocarbons (*6–8*), and various inorganic chemical species (*9–16*), in vapor (*16, 17*) and condensed phases.

Several investigators have studied the behavior of trace elements during coal combustion. Davison (*18*) proposed a mechanism whereby volatile species are enriched in respirable, fine particles through vaporization in the combustion zone followed by condensation on particle surfaces. Kaakinen et al. (*9*) and Klein et al. (*11*) demonstrated enrichment of elements in emitted particles resulting from the greater penetration of fine, highly enriched particles through emission control devices. Others (*1, 12, 14, 15, 18*) observed similar

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enrichments by these mechanisms in small particles emitted from coal combustion. However, comprehensive studies of trace element emissions from the combustion of U.S. coal have been reported for only a few utility-scale generating units. These include Unit No. 5 of the Valmont Power Station (*9*), the T. A. Allen Steam Plant (*11*), and the Chalk Point Plant (*12*). Most of the plants studied burn Eastern and Illinois coals, and relatively few studies have been made of plants burning low-sulfur, Western coal. Thus, in general, the specific effects on emissions of coal type, differences in the chemical form and physical distribution of coal constituents, and emission-control devices have not been adequately determined.

Furthermore, insufficient attention has been given to measuring particle-distribution parameters, especially in submicrometer particles. The emission of fine particles is of special interest because these particles often contain high concentrations of potentially toxic substances in thin, surface layers (*19*) and can be deposited efficiently in the pulmonary alveoli (*20*).

In this paper, we report the results of tests on power units at two conventional, large, western, coal-fired power plants (referred to as plants A and B), one burning low-sulfur bituminous coal, the other burning low-sulfur subbituminous coal. Cold-side electrostatic precipitators (ESP) were used to control particulate emissions at both plants.

Experimental

Plant Description and Sample Collection. At plant A, we tested a 430-MW (net electrical) coal-fired steam electric generator. The unit uses tangentially fired burners and a cold-side ESP with an efficiency between 99.5 and 99.8%. The unit burns ~1.45×10^5 kg of pulverized (200-mesh) western bituminous coal per hour, with ash, sulfur, and heat contents of 9.2%, 0.46%, and 28660 J/g, respectively, on a dry basis (moisture content was 6.8%). Stack gases exit through a 183-m stack.

Four filter and seven impactor samples were collected isokinetically in stack at the 91-m level during a 1-week period in January 1975. Sampling times ranged from 55 min to 3 h, the stack temperature was 117 °C, stack pressure ranged from 1.12 to 1.87 mmHg (gauge), and stack-gas velocity ranged from 23.9 to 25.9 m/s. Velocity-traverse data showed that the velocity profile was flat 91 cm beyond the inside wall. Flow rates through both impactor and filter samplers ranged from 10.8 to 16.1 L/min (wet gas volume).

At plant B, the 750-MWe ESP-equipped unit uses opposed front- and rear-fired burners. Flue gases leaving the boiler flow through two cold-side ESPs arranged in a chevron design before exiting through a 91-m stack. Each precipitator is four units wide and four mechanical sections long and has a specific collecting area of 4760 cm^2/m^3. When all sections are operating properly, net particle-removal efficiency of the ESP system at full load is rated at 97%.

Samples were collected in-stack at the 61-m level of the ESP-equipped unit during July 1975 (*21*). The gross load varied from 515 to 715 MWe, but was constant during each test. Four of the 32 separate electrical precipitator sections were inoperative during most of the test period. Precipitator efficiency in removing total suspended particles (TSP) under the test conditions was estimated at about 97% (see below). Eight filter and ten cascade impactor samples were collected. Additional samples, including simultaneous samples from the inlet, outlet, and plume (*15*), were collected during February 1976, but are not reported here.

Samples of coal, ESP-collected ash, and bottom ash were also taken at both plants during stack fly-ash collections. At plant A, pulverized coal samples were taken hourly, each sample consisting of a 5-min sample from each of five feeding systems.

Sampling Procedures. Stack emissions were sampled at each plant, using a modified EPA sampling train as described previously (*22*). Hourly records of plant operating data, including gross generating load, coal consumption, proximate analyses, energy-conversion factors (daily at plant A, monthly at plant B), and status of ESP sections, were obtained at both plants. Velocity, temperature, and pressure of the stack gas were monitored continuously during each collection. Filter samples were collected on 47-mm, 0.4-μm Nuclepore filters. Impactor samples were collected with 7- and 11-stage University of Washington Mark III and Mark V source test cascade impactors, using polyethylene or polycarbonate collection substrates and 47-mm, 0.4-μm Nuclepore backup filters. Impaction substrates were coated with a vacuum grease to improve the collection efficiency.

Analyses. In addition to gravimetric analyses, up to 43 elements were analyzed in stack samples, ESP-collected ash, bottom ash, and coal by instrumental neutron activation analysis (INAA) as described previously (*23, 24*). Cadmium and Be were analyzed in coal and fly ash, and Pb, Cd, and Be were analyzed in filter and cascade impactor samples, all with a Perkin-Elmer Model 603 atomic absorption spectrometer equipped with a Perkin-Elmer Model 2100 heated graphite analyzer. Samples were dissolved in a mixture of perchloric, nitric, and hydrofluoric acids after ashing overnight at 450 °C. Mercury in coal was analyzed by flameless atomic absorption techniques similar to those of Murphy (*25*). Nickel, Pb, and Cd were measured in bulk coal and fly-ash samples with energy-dispersive X-ray fluorescence analyses (XRF). Coal samples for XRF were dry ashed at 450 °C overnight, ground to 30 to 60 μm, and pressed into pellets with an equal amount of Avicel binding agent. γ rays from ^{109}Cd were used to excite characteristic fluorescent X-rays. The measurement and analyses of spectra are described by Bonner et al. (*26*). Results from each of these techniques were verified with NBS standard reference materials (SRM) 1632 (coal) and 1633 (coal fly ash), which were analyzed along with the samples, and through interlaboratory comparisons of results on SRM samples (*27*) and size-classified fly-ash fractions (*28*).

Computation of Coal Consumption and Atmospheric Discharge Rates. Rates of coal consumption were computed from data provided by plant personnel. At plant A, the coal consumption rate was measured by the plant-metering system and at plant B it was computed from the gross electrical generating load, the known heat-to-electrical conversion factor (a monthly average), and the heat content of the coal as described previously (*21*). Input rates of constituent elements were obtained by multiplying their concentrations in coal (listed in Table I) by the rate of coal consumption. Typical rates of coal consumption at each of the units are listed in Table II.

Rates of atmospheric discharge of minor and trace element species were computed using the measured stack concentrations and stack-gas velocities. Because the quantities of coal consumed, electric power produced, and energy-conversion factors of the units differed, comparison of the emission data is facilitated by normalizing the data to the amount of heat input into the boiler. The heat input was computed from the metered coal-flow rate and the heat content of the coal for the unit at plant A and from the gross generating load and energy-conversion factor for the unit at plant B. The energy-conversion factors are listed in Table II.

Results and Discussion

Distributions of Total Suspended Particles. Parameters used to calculate the total aerosol emitted from each of the two plants were obtained by counting particles on filter samples

Table I. Concentrations of Elements in Coal Burned at Two Western Power Plants, $\mu g/g$

	Plant A	Plant B	
	Jan 75	July 75	Feb. 76
Al	7072 ± 360 (5)[a]	30300 ± 3600 (15)[a]	29500 ± 2390 (7)[a]
Ag	0.250 ± 0.026 (1)	–	
As	0.583 ± 0.087 (12)	2.73 ± 0.71 (11)	2.84 ± 0.84 (5)
Ba	78.5 ± 9.2 (12)	418 ± 88 (14)	420 ± 167 (7)
Be[b]	0.32 ± 0.11 (6)	1.6 ± 0.5 (9)	1.2 ± 0.6 (7)
Br	–	0.96 ± 0.18 (2)	–
Ca	6100 ± 470 (5)	5360 ± 730 (15)	5620 ± 860 (7)
Cd[b]	0.14 ± 0.025 (5)	0.061 ± 0.019 (10)	0.17 ± 0.02 (7)
Ce	8.93 ± 0.22 (12)	25.6 ± 1.7 (15)	27.0 ± 2.0 (7)
Cl	73 ± 18 (5)	71 ± 20 (4)	48 ± 17 (1)
Co	0.840 ± 0.040 (12)	1.98 ± 0.25 (14)	2.08 ± 0.22 (7)
Cr	7.74 ± 0.33 (12)	5.19 ± 0.29 (15)	7.02 ± 1.28 (7)
Cs	0.454 ± 0.012 (5)	0.70 ± 0.08 (15)	0.72 ± 0.16 (7)
Cu	6.68 ± 0.22 (5)	13.4 ± 1.2 (6)	12.7 ± 0.6 (7)
Dy	0.54 ± 0.02 (5)	1.63 ± 0.13 (15)	1.60 ± 0.09 (7)
Eu	0.101 ± 0.005 (5)	0.250 ± 0.009 (14)	0.261 ± 0.018 (7)
Fe	2860 ± 120 (12)	5720 ± 380 (15)	6470 ± 570 (7)
Ga	2.67 ± 0.50 (12)	8.8 ± 1.4 (11)	8.48 ± 1.25 (7)
Hf	1.14 ± 0.10 (5)	2.23 ± 0.12 (15)	2.38 ± 0.11 (7)
Hg	0.11 ± 0.01 (5)	0.065 ± 0.015 (5)	0.10 ± 0.02 (5)
In	0.010 ± 0.002 (3)	0.0415 ± 0.0046 (13)	0.039 ± 0.006 (5)
K	764 ± 45 (5)	1820 ± 250 (14)	1730 ± 261 (7)
La	5.09 ± 0.34 (5)	14.3 ± 0.8 (15)	13.4 ± 0.8 (7)
Lu	0.062 ± 0.015 (5)	0.239 ± 0.009 (14)	0.23 ± 0.03 (6)
Mg	1025 ± 109 (5)	2330 ± 470 (11)	2240 ± 753 (6)
Mo	1.17 ± 0.05 (5)	2.60 ± 0.54 (15)	2.67 ± 0.26 (6)
Mn	13.3 ± 3.4 (9)	54.1 ± 1.6 (15)	60.2 ± 20.0 (7)
Na	2330 ± 70 (5)	2940 ± 160 (15)	2930 ± 248 (7)
Nd	3.98 ± 0.20 (5)	9.86 ± 0.90 (15)	10.6 ± 1.1 (7)
Ni[c]	2.99 ± 0.45 (5)	–	–
Pb[c]	2.52 ± 0.13 (5)	10.2 ± 1.2 (16)	12.1 ± 0.7 (7)
Rb	4.03 ± 0.32 (5)	9.05 ± 0.53 (15)	12.1 ± 1.8 (7)
S[d]	4600 ± 100 (5)	5200 ± 800 (2)	5800 ± 600 (12)
Sb	0.160 ± 0.011 (5)	0.572 ± 0.049 (15)	0.614 ± 0.095 (7)
Sc	1.46 ± 0.09 (12)	2.77 ± 0.11 (15)	2.98 ± 0.20 (7)
Se	1.47 ± 0.09 (12)	1.55 ± 0.15 (15)	1.74 ± 0.25 (7)
Sm	0.659 ± 0.013 (12)	1.71 ± 0.17 (15)	1.81 ± 0.16 (7)
Sr	67.0 ± 2.7 (5)	87.2 ± 8.9 (15)	97.7 ± 8.3 (7)
Ta	0.160 ± 0.006 (5)	0.492 ± 0.038 (15)	0.513 ± 0.056 (7)
Tb	0.0810 ± 0.003 (5)	0.165 ± 0.009 (15)	0.22 ± 0.02 (7)
Th	1.65 ± 0.03 (5)	5.73 ± 0.32 (15)	6.21 ± 0.67 (7)
Ti	483 ± 82 (5)	1220 ± 200 (14)	1230 ± 176 (6)
U	0.573 ± 0.023 (5)	1.85 ± 0.19 (15)	2.12 ± 0.25 (7)
V	9.8 ± 1.2 (12)	22.1 ± 3.2 (9)	24.9 ± 3.1 (4)
W	–	0.80 ± 0.24 (5)	<0.13 (1)
Yb	0.368 ± 0.022 (5)	0.817 ± 0.060 (15)	0.84 ± 0.06 (7)
Zn	7.16 ± 0.29 (5)	14.7 ± 1.7 (15)	16.4 ± 3.2 (7)
Zr	40.5 ± 6.5 (5)	52.2 ± 5.9 (15)	66.7 ± 9.8 (7)

[a] Number of replicate samples. [b] Measured by atomic absorption spectroscopy. [c] X-ray fluorescence. [d] Sulfur analyses provided by plant personnel; all others measured by instrumental neutron activation analysis.

Table II. Typical Rates of Coal Consumption and Energy-Conversion Factors

	% Full load	Coal rate (g/s)	Energy-conversion factor (Btu/kWh)
Plant A	98	3.98×10^4	9.25×10^3
Plant B	94	9.71×10^4	9.47×10^3
	82	8.57×10^4	9.38×10^3

Table III. Size-Distribution Parameters of Total Stack-Emitted Aerosols Determined from Scanning Electron Microscopy Analyses of Nuclepore Filter Samples

	Small-Particle Mode				Large-Particle Mode			
	NMD[a]	VMD[b]	MMAD[c]	σ_g^d	NMD[a]	VMD[b]	MMAD[c]	σ_g^d
Plant A	0.065	0.088	0.14	1.37	0.565	1.04	1.6	1.57
Plant B	0.055	0.084	0.13	1.42	0.74	5.2	8.1	2.2

[a] Number median diameter (μm). [b] Volume median diameter (μm) determined by $\ln VMD = \ln NMD + 3 \ln^2 \sigma_g$. [c] Estimated mass median aerodynamic diameter (μm), using particle densities of 2.2 and 2.44 g/cm^3 for plants A and B, respectively. [d] Geometric standard deviation of assumed log normal distribution.

via scanning electron microscopy (SEM) techniques (see ref 22) and are given in Table III. The distributions were in each case bimodal, with distinct modes in sub- and supermicrometer size ranges. The submicrometer mode is composed of aggregates of smaller particles that may be formed in part from vapor condensation and bubble-bursting mechanisms. These particles are too small to be collected by our impactor and, ignoring wall losses and boundary effects in the impactor, are deposited totally on the backup filter. The second mode contains much larger, mostly solid, spherical particles derived mainly from residual mineral matter in coal (*29–31*). Urlich (*30*) observed similar particle-distribution modes and suggested that the particles in the smaller mode are largely condensed, volatile Si compounds and metal oxides.

Median diameters of the smaller particles from both units are almost identical. Median diameters of the larger particles (see Table III) strongly reflect differences in the overall collection efficiency of the control device. The smaller median diameters of the large particles emitted at plant A indicate a greater collection efficiency of the larger particles. Optimum collection efficiencies of the plant A and plant B ESP systems are 99.7 and 97.5%, respectively.

Impactor Data. In Figures 1A through E, we have plotted typical particle-size distributions of elements collected in cascade impactor samples that were placed in-stack and downstream from the ESP-equipped units at each plant. The emission factors (ng/J heat input) of several elements are plotted vs. the aerodynamic diameters of particles. Physical diameters were determined by sizing particles on impactor stages and backup filters via SEM and transformed to aerodynamic diameters using the particle density and slip-correction factor (*32*). We corrected the mass of each element present on backup filters by the excess mass resulting from bounce off and reentrainment of large particles as described previously (*22*). Thus, we can estimate more accurately the fraction of each element emitted in submicrometer particles.

Significant amounts of several elements, including V, W, Ga, Mo, Ca, Br, Ba, Se, As, Sb, U, Fe, Cr, Zn, Co, and Mn, were emitted in submicrometer particles. The fraction of other elements in submicrometer particles is generally much less, but too small to determine accurately (*22*).

We attempted to evaluate wall losses by comparing concentrations in impactor and filter samples; because of the variation between successively collected samples, accurate comparisons could not always be made. In general, however, concentrations of elements in the flue gas, which were determined by summing the amounts on impactor stages, were typically from 10 to 60% lower than concentrations on filters in samples from the ESP at plant A and from 12 to 40% lower in samples from the ESP at plant B. The magnitude of the discrepancy depended on the specific element, its distribution among particle sizes, and sampling time (see ref *22*).

Aerosol-Distribution Parameters of Minor and Trace Elements. Elemental mass median aerodynamic diameters (EMMAD) were determined from analyses of cascade impactor samples collected at each of the units and they are listed in Table IV. These data reflect only the larger particle modes. Ranges of median EMMADs of particulate emissions from the plant A and plant B ESP units were 1.8–4.9 and 4.3–12.1 μm, respectively. Thus, as in the case of the total aerosol (see Table III), the EMMADs of particles from the more efficient ESP were smaller.

Elements in emissions from each of the units show distinct behavior in their distributions according to particle size. At plant A, the distributions of Al, Ce, Cl, Fe, Hf, K, La, Na, Sc, and Th were nearly identical. The EMMADs of particles containing As, Ba, Ga, I, U, V, W, and Zn were about half those of particles with elements in the Al group. The EMMADs of Co, Cs, Cu, Mo, Mn, and Sb were slightly smaller than those containing the Al group. If an element were distributed on only the surfaces of aerosol particles, then its mass distribution would coincide with the surface-area distribution of the aerosol. The calculated surface-area median aerodynamic diameters (SMAD) of elements in the Al group (about 1.8 for particles having an EMMAD of 2.5 μm and σ_g of 2.3) are nearly equal to the EMMADs of elements in the As group, thus indicating surface occurrence of elements in the As group on particles containing elements in the Al group. This would occur if these elements were deposited from the vapor phase;

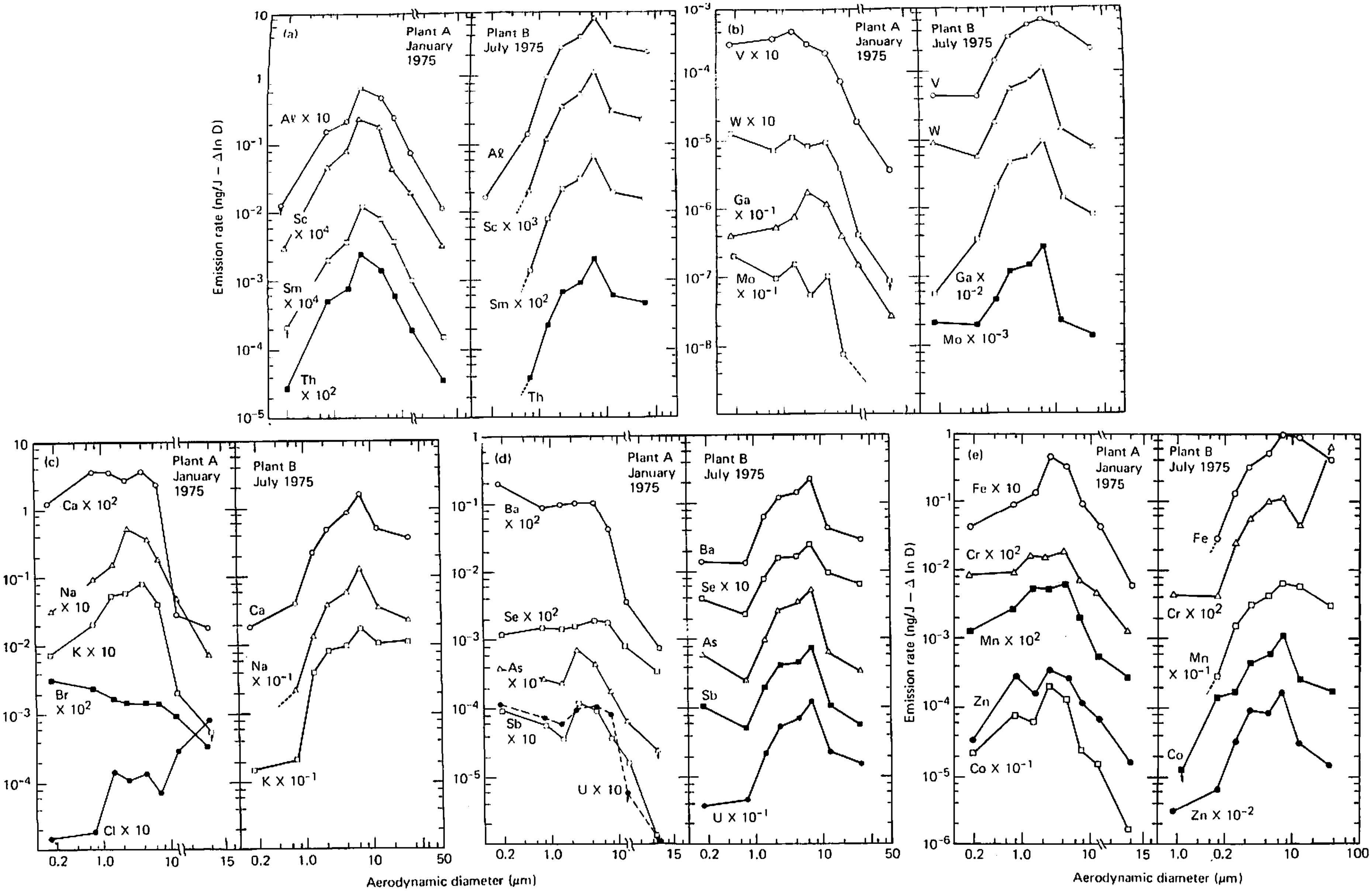

Figure 1. Typical distributions of mass vs. particle size of elements in aerosols emitted from two coal-burning steam-generating units. Masses of elements are expressed as emission rates per joule of heat input to the boiler as discussed in the text

however, the computation is quite sensitive to the value of the σ_g.

Median EMMADs of rare earths, Al, Fe, Co, Cr, K, Mg, Ti, Zr, and Sc, emitted from the ESP unit at plant B (Table IV) ranged from about 9 to about 12 μm; those containing As, Ba, Ga, In, Mo, Sb, U, V, W, and Zn ranged from about 4 to 6 μm, or about half those containing elements in the Al group and near the SMADs, i.e., 5.1 μm for MMAD of 8.87 μm and σ_g of 2.87, of particles with elements in the Al group. The EMMADs of Ca, Na, Sr, and Se were generally intermediate between those containing the As and Al groups.

On comparing the EMMADs of particles emitted from ESP units at the two plants, elements in the large particle mode from plant A seem to be distributed somewhat more heterogeneously than elements in the corresponding mode from plant B. Rather high EMMADs were often observed for particles containing Br, Cl, and I (4.0, 15, and 3.7 μm, respectively) in aerosol particles from the ESP at plant A, and for Se-containing particles (5.8 μm at plant A and 9.5 μm at plant B) in aerosols from both plants. These elements are the most volatile of the elements detected, and the high EMMADs may result from the adsorption of vapors either by large porous particles or by impactor substrates. In the latter case the data may be in error. Studies to determine the importance of adsorption of vapor-phase elements on impaction substrates are in progress at our laboratory.

Partitioning and Atmospheric Emission of Elements. In Table V we list emission factors (pg/J) of elements in samples from plant A. As noted above, wall and interstage losses were severe in impactor samples collected from these ESP units. Therefore, the emission factors of elements were derived only from filter samples.

For data from plant B, instead of median values, we report values determined from a sample collected while the unit was operated at 625 MW (about 80% load). During all tests, four ESP sections were inoperative; however, the unit was operated in compliance with emission standards by reduction of the gross generating load. By far, the lowest emissions were measured consistently from plant A. Emissions from the Valmont Unit 5 (*9*) and Allen Steam Plant (*11*) (not shown) were generally in the range between those of plants A and plant B.

Further normalization of the data in Table V by dividing by the input rates of the elements in coal (expressed in ng/J) yields the penetration of each element through the boiler and ESP. Penetrations of elements are independent of their concentrations in coal and are listed in Table VI for both of the generating units.

Penetrations varied considerably, as did emissions, with the element and specific power unit. In general, the lowest pene-

Table IV. Elemental Mass Median Aerodynamic Diameters of Aerosols from Two Coal-Fired Electrical Generating Units, μm

Plant A January 1975 Elements	EMMAD[a]	σ_g[b]	Plant B July 1975 Elements	EMMAD[c]	σ_g[b]
Ta, Tb, Sc	~4.5	1.4 - 2.8[d]	Cr, Cs, Rb, Zr	~12	2.2 - 3.0
Sm, Nd, Mg, Lu, Yb, In, Eu	~3.3	1.4 - 2.4 3.0[d]	Al, Br, Ce, Co, Dy, Eu, Fe, Hg, K, La Lu, Mg, Nd, Sc, Sm, Ta, Tb, Th, Ti	~9.5	2.2 - 3.2
Hf, K, La, Sc, Th Al, Ce, Cl, Na	~2.5	1.6 - 2.7[d] 1.8 - 2.3	Ca, Mn, Na, Se	~8.2	2.7 - 3.5
Ca, Mo, Sb, Cu, Mn Co, Cs, Rb, Ti, Fe	~2.3	1.5 - 2.6	As, Ba, Ga, In Mo, Sb, U, V, W, Zn	4.4 - 6.3	1.9 - 3.4
Br, Cr, U, W, Zn Ga, Sr, I, As, Ba, V	~1.7	1.5 - 2.0 (2.1 - 3.7)[d] 1.5 - 2.3 (2.1 - 4.2)[d] 1.6 - 2.9			

[a] EMMADs estimated from up to five impactor samples. The relative standard deviation of successive determinations of the EMMADs was typically about 20%, but errors among elements are typically ≤10%. [b] Geometric standard deviation. [c] Range of median values of EMMADs of up to six impactor samples for each element. [d] Value corresponds to element underlined.

Table V. Emission Factors of Elements in Particles from Generating Units at Two Coal-Fired Power Plants (pg/J)[a]

	Plant A January 1975 Median	Minimum	Maximum	Plant B ESP Unit July 1975 625-MW Sample[b]	Minimum	Maximum
Al	320 ± 13	286	354	15,600 ± 500	3860	21,700
As	0.22 ± 0.014	0.15	0.22	15.3 ± 0.3	5.77	15.3
Ba	10.8 ± 1.6	10.3	11.1	807 ± 10	243	807
Be	–			0.72 ± 0.24	0.42	0.72 (3)
Br	0.125 ± 0.035	0.091	0.20	6.6 ± 3.5		(1)
Ca	216 ± 35 (2)	188	243	3400 ± 100	1590	3940
Cd	–			0.26 ± 0.04	0.097	0.26 (4)
Ce	0.48 ± 0.02	0.41	0.52	16.0 ± 0.5	8.25	21.3
Cl	0.98 ± 0.42	0.37	1.7	–		
Co	0.10 ± 0.01	0.084	0.11	2.38 ± 0.04	1.12	3.05
Cr	0.81 ± 0.07	0.68	1.0	9.58 ± 0.36	3.1	30.5
Cs	0.042 ± 0.002	0.036	0.068	0.410 ± 0.031	0.209	0.615
Dy	–			1.12 ± 0.03	0.324	1.52
Eu	0.0061 ± 0.0004	0.0047	0.0070	0.164 ± 0.005	0.0847	0.218
Fe	156 ± 7	130	187	3670 ± 40	1980	5350
Ga	0.59 ± 0.18	0.49	0.63	18.7 ± 1.0	9.74	19.8
Hf	–			1.37 ± 0.03	0.717	1.85
I	3.5 ± 0.3	3.2	4.4	–		
In	0.0024 ± 0.00014	0.0023	0.0031	0.108 ± 0.008	0.0339	0.108
K	43 ± 20	26	46	905 ± 200	441	1130
La	0.26 ± 0.014	0.22	0.32	8.96 ± 0.09	4.75	12.0
Lu	0.0032 ± 0.0004 (2)	0.0029	0.0036	0.164 ± 0.007	0.0701	0.231
Mg	–			1360 ± 380	1170	3240
Mo	0.079 ± 0.010	0.057	0.15	6.48 ± 0.76	2.26	8.61
Mn	0.45 ± 0.03	0.42	0.47	41.2 ± 0.5	9.07	41.2
Na	121 ± 5	77	160	2210 ± 10	1120	2810
Nd	0.21 ± 0.06	0.13	0.21	6.05 ± 0.48	3.42	8.40
Rb	0.37 ± 0.12 (1)			5.52 ± 0.57	2.52	7.52
Sb	0.052 ± 0.003	0.048	0.054	2.15 ± 0.04	0.863	2.15
Sc	0.074 ± 0.0014	0.061	0.084	1.96 ± 0.02	1.03	2.72
Se	0.26 ± 0.02	0.14	0.27	5.82 ± 0.16	2.83	6.07
Sm	0.033 ± 0.002	0.029	0.036	1.14 ± 0.06	0.648	1.60
Sr	5.4 ± 0.8 (1)			85.4 ± 8.0	32.2	111
Ta	0.0077 ± 0.0014	0.0056	0.0098	0.323 ± 0.13	0.158	0.441
Tb	0.0042 ± 0.0005 (2)	0.0036	0.0047	0.112 ± 0.006	0.060	0.158
Th	0.082 ± 0.004	0.065	0.091	3.67 ± 0.06	1.96	5.09
Ti	24 ± 8 (2)	17	31	892 ± 90	338	1150
U	0.091 ± 0.014	0.084	0.10	3.29 ± 0.15	1.39	3.29
V	0.99 ± 0.04	0.65	1.8	39.7 ± 3.2	17.3	39.7 (5)
W	0.091 ± 0.009 (1)			2.78 ± 0.18	1.20	2.78
Yb	–			0.503 ± 0.019	0.271	0.789
Zn	1.6 ± 0.14	1.2	1.8	44.8 ± 2.4	16.5	44.8
Zr	1.6 ± 0.7 (1)			34.6 ± 7.1	13.1	41.1

[a] All values are based on analyses of filter samples only and were calculated on a dry gas basis at standard temperature and pressure. The water vapor contents of stack gasses were 9.2 and 7.9% at plants A and B, respectively. The data reflect three and six samples for plants A and B, respectively, or the number in parentheses. Uncertainties reported are analytical uncertainties only; the total uncertainty in any given determination is typically about 20%. [b] Results of a single sample collected when the unit operated at 83% capacity and with four precipitator sections inoperative.

Table VI. Penetration of Elements Contained in Particles through the Boilers and ESPs at Two Coal-Fired Power Plants (%)

Plant A Element	Penetration[a]	Plant B Element	Penetration[b]
Br, Cl	0.029, 0.006	Br	0.34
Al, Ti, Mn, K Ca, Hf, Ta, Yb	0.07 - 0.13	Al, Sc, Lanthanides Th, Ti, Ta, Fe, Be, Mg, Ca, Na, K, Rb	0.9 - 1.6
Sm, La, Th, Ce Fe, Sc, Na, Lu Sr, Cs	0.14 - 0.24	Mn, Co, Cr	1.6, 2.5, 3.8
V, Cr, Ba, Co	0.29 - 0.40	U, V, Ba, Ga, Mo, Pb, In	3.7 - 5.5
U, Se, Ga	0.53, 0.56, 0.65		
Zn, In, Sb, As	0.78 - 1.1	As, Cd, Se, Sb, W, Zn	6.3 - 11.5

[a] Range of median values of up to six samples. [b] Range of median values of up to eight samples. Penetration is defined as [atmospheric emission factor (ng J^{-1})/input (ng J^{-1})] × 100 (see text).

fractions were observed for lanthanides, Th, Zr, some alkali metals, Sc, and Al, all of which tended to be in particles with the largest MMADs (see Table IV) and are associated largely with fly ash resulting from penetration of residual mineral matter. Elements associated with smaller particles, i.e., those in the As group, typically had the largest penetrations. Penetrations of Br and Cl were quite low relative to other elements. Klein et al. (*11*) and others suggested that significant quantities of some highly volatile elements such as Br, Cl, Se, and Hg have significant gas-phase components. Indeed, a rough mass balance indicates that between 7 and 35% of the Se contained in coal is emitted from plant B in the vapor phase.

Median penetrations of elements in large particles were about 0.2% at plant A and about 1.4% (625-MW sample) at plant B. These values correspond to 99.8 and 98.6%, respectively, for the net removal efficiency of these elements. At both plants, about 20% of the ash is removed from the boiler as bottom ash, and the remaining 80% enters the emission-control systems. Given the efficiency of the ESPs at the two plants (99.7 and 97.5% for the total aerosol), the net efficiencies for the removal of total aerosol of the bottom-ash–ESP systems are 99.8 and 98.5% at plants A and B, respectively. The removal efficiencies of elements and total aerosol agree very closely at both plants. This indicated that only a small portion of the mass of elements is contained in fine particles that have higher penetrations.

Thus, the penetration of elements associated with the large-particle fly-ash mode that is derived from residual mineral matter and termed lithophilic by Klein et al. (*11*) is nearly equal to the penetration of the total aerosol. As noted by Klein et al. (*11*), the penetrations of what appear to be the more mobile elements (classified as calcophiles by Klein et al. (*11*)) that occur in small particles are much higher, their concentrations thereby becoming enriched in the total aerosol relative to the nonmobile matrix elements. The enrichment of elements in the combustion process and in systems for the removal of fly ash may be expressed by the ratio of the penetration of a given element to that of the total aerosol or to that of an element whose penetration is similar to the total aerosol. The ratios of penetrations of each of the elements to that of Sc are listed in Table VII for the two plants and plotted vs. particle diameter in Figure 2. Because of this internal normalization, the penetration ratios are identical with an enrichment factor obtained via double normalization of the concentrations of elements in in-stack fly-ash and coal samples. We will refer to the penetration ratios or enrichment factors as relative penetrations (RP). Relative penetrations are affected by the distribution of the element among particle sizes, vapor–particulate fractionation of the element, and the particle-size collection-efficiency curve of the control system.

Relative Penetration vs. Particle Size. As suggested by Gladney et al. (*12*), the elements may be classified conveniently on the basis of the curves of the relative penetration (or enrichment factor) vs. particle size. At plant A, these curves for the lanthanides, K, Ti, Mg, Cs, Rb, Hf, Ta, Sc, and Mn were similar to that for Th (Figure 2a). These show no change in concentration throughout the size range of particles. Curves for Ce, Na, Sr, and Fe were similar to those of the Th group, but were slightly enriched in the smallest sized particles. The curves for K and Ti are similar to that for Fe, but are displaced below Sc (≡1) in relative penetration. The penetration of Ca (Figure 2a) was less than that of Sc, i.e., RP < 1, in larger particles, but greater in smaller particles.

At plant A, the curves of RP vs. particle size for V, Sb, and As were similar to that of Ba (Figure 2a). The RPs of these elements on small particles were the largest observed. Several elements, including Br, Se, Cr (Figure 2b), Mn, Ta, Co, and to a lesser extent Zn, were definitely enriched in larger particles as well as in smaller particles. Gladney et al. (*12*) observed similar enrichments of Se and Hg in large particles. Significant quantities of Se, Hg, and Br are in the vapor phase in flue gasses and may have been adsorbed onto impactor substrates, on large porous particles, or on large carbonaceous particles, which we saw on the upper stages of impactors collected at plant A.

Curves of RP vs. particle size for elements in plant B aerosols are shown in Figure 2c. Curves for the lanthanides, K, Hf, Th, Ti, Mg, Cs, Rb, Ta, Sc, and Mn were similar to those for Na and Fe. These showed little or no enrichment in any sized particle. Enrichments of W, U, Ba, Zn, V, In, Ga, Ba, As, Se, Sb, and Mo are considerable and increase with decreasing particle size. Curves for these elements tended to be somewhat bimodal (see W) with a broad maximum between 2 and 10 μm (see W, U, and Ba in Figure 2b). The curves for Se differ somewhat from those of W, U, and Ba in that the minimum is broader. Both Cr and Co (Figure 2c) were highly enriched in the smallest sized particles, but the curves of RP vs. size were distinctly different from those of elements with curves similar to W.

Relative Penetration of Elements. In column 4 of Table VII we list RPs of elements from five samples collected at plant B when the load was 515 or 530 MW. Despite the rather large range in the absolute elemental emission rates (typically twofold or more, see Table V), the penetration ratios of the

Table VII. Relative Penetration of Elements [a] in Aerosols from Several Coal-Fired Power Plants

	This Work			Other Studies		
	Plant A Average[b]	Plant B				
		625 MW[c]	515–530 MW[d]	Allen[e]	Chalk Point[f]	Valmont[g]
Sb	7.0 ± 2.0	5.3 ± 1.0	4.0 ± 0.7	6.7	4.0	–
Cd	–	6.0 ± 2.1	–	–	–	–
W	–	4.9 ± 3.0	3.7 ± 1.3	–	–	–
As	6.6 ± 1.2	7.9 ± 4.1	5.7 ± 1.0	6	6.3	–
In	5.5 ± 2.2	3.7 ± 1.0	2.6 ± 0.7	–	–	–
Zn	4.3 ± 1.2	4.3 ± 1.1	3.0 ± 0.5	7.8	1.5	2.5
Pb	–	3.8 ± 1.5		8.1	3.7	3.1
Ga	4.3 ± 1.6	3.0 ± 1.0	2.8 ± 0.6	–	1.2	–
U	3.3 ± 0.5	2.5 ± 0.6	1.9 ± 0.15	–	–	–
Se	3.0 ± 1.4	5.3 ± 1.2	4.5 ± 0.7	5.5	5.7	1.7
Ba	2.5 ± 0.6	2.7 ± 1.1	1.8 ± 1.0	0.7	0.92	–
Cr	2.5 ± 0.4	2.6 ± 0.4	1.75 ± 0.26	3.0	1.1	–
Co	2.3 ± 0.2	1.7 ± 0.4	1.5 ± 0.1	1.4	1.0	–
V	2.0 ± 1.5	2.5 ± 0.8	2.2 ± 0.7	2.5	0.75	–
Mo	1.8 ± 1.4	3.5 ± 1.7	2.7 ± 0.9	–	–	3.0
Rb	1.8 ± 0.7	0.89 ± 0.16	0.81 ± 0.09	0.75	–	0.94
Cs	1.7 ± 0.4	0.82 ± 0.28	0.80 ± 0.14	1.5	–	–
Sr	1.2 ± 0.2	1.4 ± 0.4	1.3 ± 0.3	1.0	–	–
Eu	1.2 ± 0.15	0.92 ± 0.12	0.92 ± 0.08	0.79	0.75[h]	–
Mg	1.1 ± 0.2	0.8 ± 0.5	1.5 ± 0.6	0.54	–	–
Fe	1.1 ± 0.1	0.90 ± 0.14	0.94 ± 0.02 (0.05)	0.84	0.83	≡1.0
Ce	1.06 ± 0.07	0.88 ± 0.14	0.86 ± 0.02 (0.05)	–	0.75[h]	–
Na	1.0 ± 0.2	1.1 ± 0.15	1.1 ± 0.2	0.99	1.0	–
Sc	≡1.00 ± 0.13	≡1.00 ± 0.12	≡1.00 ± 0.12	≡1.0	≡1.0	–
Lu	1.0 ± 0.4	0.97 ± 0.14	0.97 ± 0.02	–	0.75[h]	–
La	1.0 ± 0.1	0.88 ± 0.12	0.86 ± 0.06	0.68	0.75[h]	–
Yb	–	0.89 ± 0.16	0.94 ± 0.05	–	0.75[h]	–
Hf	–	0.87 ± 0.12	0.86 ± 0.04	0.76	–	–
Sm	1.0 ± 0.15	0.96 ± 0.29	0.97 ± 0.05	0.55	0.75[h]	–
K	1.0 ± 0.4	0.7 ± 0.3	0.68 ± 0.10	0.95	0.83	–
Tb	0.97 ± 0.19	0.96 ± 0.16	0.93 ± 0.11	–	0.75[h]	–
Ta	0.95 ± 0.27	0.89 ± 0.16	0.88 ± 0.06	1.0	–	–
Th	0.95 ± 0.19	0.90 ± 0.13	0.90 ± 0.03	0.76	–	–
Ti	0.91 ± 0.18	1.0 ± 0.1	0.9 ± 0.3	1.2	0.75	–
Al	0.86 ± 0.07	0.75 ± 0.16	0.73 ± 0.08	0.44	0.83	0.94
Nd	0.84 ± 0.22	0.89 ± 0.28	0.91 ± 0.07	–	0.75[h]	–
Ca	0.76 ± 0.19	0.89 ± 0.28	0.81 ± 0.12	–	0.92	–
Zr	0.7 ± 0.3	0.96 ± 0.42	0.91 ± 0.18	–	0.83	0.73
Mn	0.68 ± 0.17	1.1 ± 0.7	0.85 ± 0.25	0.78	–	–
Be	–	0.6 ± 0.4	–	–	0.64[i]	–
Br	0.2 ± 0.1	0.1 ± 0.1	–	–	0.17	–

[a] Penetration (Table VI) of each element to that of Sc, which is identical with the enrichment factor used by Gladney et al. (*12*) and Gordon et al. (*33*). [b] The uncertainty reported is the larger of twice the standard deviation and twice the analytical uncertainty. Rb is based on one sample. [c] The uncertainty reported is twice the individual uncertainty in the ratio that was derived from standard deviations of replicate elemental analyses of coal and aerosol samples. [d] Uncertainties reported are twice the standard deviation of the replicate determinations; twice the root mean square of the individual uncertainties is given in parentheses if larger than the 2σ value. [e] Based on 1973 data of Klein et al. (*11*). [f] Unless indicated, values listed are based on data of Gladney et al. (*12*). [g] Derived from data of Kaakinen et al. (*9*) for the ESP-equipped unit. Data normalized to Fe. The value for Pb was based on ^{210}Pb. [h] Based on single value reported for "rare earths" in Gordon et al. (*33*). [i] Based on value of Gladney and Owens (*34*) renormalized to Sc.

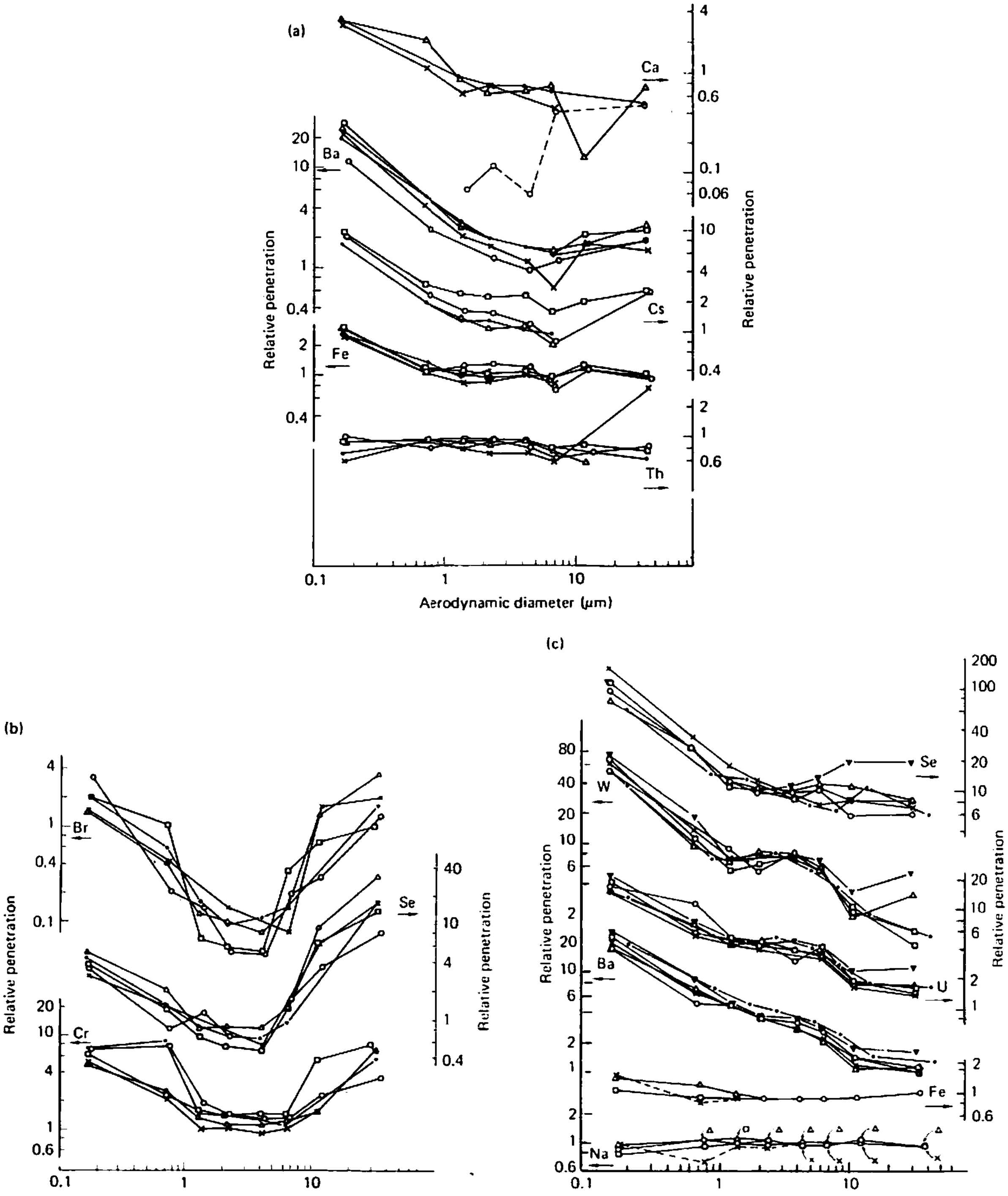

Figure 2. Relationship of relative penetration to particle size of several elements in aerosols emitted at plant A (a and b) and plant B (c). The symbols indicate different sets of data from impactors

515- and 530-MW samples varied by less than the uncertainties in the individual values (2σ typically is <20%). Thus, for a given plant it appears possible to determine the RP of elements on the basis of only a few samples. Further comparison of the penetration ratios of the 625-MW and 515- to 530-MW samples shows significant, but relatively small, differences for a few elements: As, Cr, In, Mo, and Sb. Thus, the penetration ratios of the elements seem to be relatively independent of gross generating load as well as absolute emission rate.

Despite the rather large differences in the composition and origin of the coal and differences in the combustion chambers and ESPs used at the two plants, the RPs of most of the elements were equivalent to within their respective uncertainties. In fact, except for In, Se, Mo, Rb, Cs, K, Mn, and Br, the deviation between the two values (larger/smaller × 100) was ≤35%. The largest differences in the two units were in values of In, Se, Mo, Rb, Cs, K, and Mn. Differences in RPs of the elements ranged from 1.4 for K to about 2 for Rb and Cs. However, only Rb, Cs, Mo, Se, and Mn are judged to be significantly different. The larger penetrations of Rb and Cs at plant A probably result from significantly greater concentrations of these elements in smaller particles as indicated in the curves of RP vs. particle size shown for Cs in Figure 2a. At plant B, the curves of relative penetration vs. particle size for Rb and Cs are similar to those shown for Fe and Na (Figure

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2b).

Also listed in Table VII are the RPs of elements determined at three other conventionally designed coal-fired power units equipped with cold-side ESPs. During the work of Gladney et al. (*12*), the plant at Chalk Point burned high-sulfur (1.9%) coal with an ash content of about 12%. The Valmont plant burned low-sulfur (0.6%), low-ash (6%) coal. Coal at the Allen Steam Plant contained 10.4% ash and 3.1% S (1973 data of Klein et al. (*11*)). The removal efficiences for fly ash at the Chalk Point, Valmont, and Allen Steam Plants were estimated at 97, 96.2, and 99.5%, respectively, including bottom-ash removal and other fly-ash-collection systems in addition to ESPs. Despite these differences, many of the values from these units are remarkably similar to those determined at plants A and B. The largest differences in the RPs at the five plants were those of Zn, Pb, Ba, Cr, Co, V, Rb, and Cs, which differed by as much as a factor of five. These include elements in each of the three geochemical classifications (i.e., chalophilic, Zn and Pb; lithophilic, Cs and Rb; and intermediate elements, Ba, Cr, Co, and V) described by Klein et al. (*11*). The large range in RPs of these elements is attributed to differences in distributions of elements according to particle size (and hence coal chemistry) and the removal efficiency vs. particle size curves of the ESPs.

Summary and Conclusions

The relative penetrations of several elements from two western coal-fired power plants are nearly the same, despite variations in boiler size, electrical generating capacity, precipitator size and efficiency, and coal composition, and are quite similar to those observed at plants burning high-sulfur Eastern coal. However, significant differences exist among plants in relative penetrations of the elements Zn, Pb, Ba, Cr, Co, V, Rb, and Cs. This is attributed to differences in composition of the coal and the particle size vs. efficiency characteristics of the individual ESPs. Based on concentrations of elements reported by Gluskoter et al. (*35*), enrichments relative to average crustal abundances in U.S. coals are often larger and more highly variable than enrichments (RPs) that occur during coal use in the power plants discussed above. Thus, excluding fractionation of elements that can occur in power plant plumes (*15*), the greatest impact on the final enrichment of many elements in particles emitted from these plants is due to the original coal composition. We note, however, that enrichments of elements in particles emitted from coal-burning units equipped with other types of particulate control systems such as venturi scrubbers can be much greater than those reported above (*21*).

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Literature Cited

(1) Coles, D. G., Ragaini, R. C., Ondov, J. M., *Environ. Sci. Technol.*, 12, 442 (1978).
(2) Eisenbud, M., Petrow, H. G., *Science*, 144, 228 (1964).
(3) Martin, J. E., Harward, E. D., Oakley, D. T., Smith, J. M., Bedrosian, P. H., in "IAEA Symposium on Environmental Aspects of Nuclear Power Stations, New York, 1969", IAEA Conference 700810-24, paper IAEA-Sm-146/19, 1969, pp 325-37.
(4) Hull, A. P., *Nucl. News*, 51-5 (April 1974).
(5) Moore, H. E., Martell, E. A., Poet, S. E., *Environ. Sci. Technol.*, 10, 586-91 (1976).
(6) Guerrini, R., Pennacchi, A., "La Rivista Dei Combustibili", Vol. XXIX, fasc. 7-8, Luglio-agosto, 1975.
(7) Hangebrauck, R. P., Vonlehmden, D. J., Meeker, J. E., *J. Air Pollut. Control Assoc.*, 14, 267-78 (1964).
(8) Jones, P. W., Giammar, R. D., Strup, P. E., Stanford, T. B., *Environ. Sci. Technol.*, 10, 806-10 (1976).
(9) Kaakinen, J. W., Jorden, R. M., Lawasani, M. H., West, R. E., *Environ. Sci. Technol.*, 9, 862-9 (1975).
(10) Bertine, K. K., Goldberg, E. D., *Science*, 173, 233-5 (1971).
(11) Klein, D. H., Andren, A. W., Carter, J. A., Emery, J. F., Feldman, C., Fulkerson, W., Lyon, W. S., Ogle, J. C., Talm, Y., Van Hook, R. I., Bolton, N., *Environ. Sci. Technol.*, 9, 973-9 (1975).
(12) Gladney, E. S., Small, J. A., Gordon, G. E., Zoller, W. H., *Atmos. Environ.*, 10, 1071-7 (1976).
(13) Block, C., Dams, R., *Environ. Sci. Technol.*, 10, 1011-7 (1976).
(14) Ragaini, R. C., Ondov, J. M., *J. Radioanal. Chem.*, 37, 679-91 (1977).
(15) Ondov, J. M., Ragaini, R. C., Bierman, A. H., Choquette, C. E., Gordon, G. E., Zoller, W. H., paper presented at the 173rd National Meeting of the American Chemical Society, New Orleans, March 25, 1977, Abstract ENVT-124, Lawrence Livermore Laboratory, Preprint UCRL-78825, 1977.
(16) Andren, A. W., Klein, D. H., *Environ. Sci. Technol.*, 9, 856-8 (1975).
(17) Billings, C. E., Matson, W. R., *Science*, 176, 1232-3 (1972).
(18) Davison, R. L., Natusch, D. F. S., Wallace, J. R., Evans, E. A., Jr., *Environ. Sci. Technol.*, 8, 1107-13 (1974).
(19) Linton, R. W., Loh, A., Natusch, D. F. S., Evans, C. A., Jr., Williams, P., *Science*, 191, 852-4 (1976).
(20) Task Group on Lung Dynamics, *Health Phys.*, 12, 173-208 (1966).
(21) Ondov, J. M., Ragaini, R. C., Biermann, A. H., "Elemental Emissions From a Coal-Fired Power Plant: Comparison of a Venturi Wet Scrubber-System with a Cold-Side Electrostatic Precipitator," Lawrence Livermore Laboratory, Preprint UCRL-80110.
(22) Ondov, J. M., Ragaini, R. C., Biermann, A. H., *Atmos. Environ.*, 12, 1175 (1978).
(23) Ragaini, R. C., Heft, R. E., Garvis, D., "Neutron Activation Analysis at the Livermore Pool-Type Reactor for the Environmental Research Program", Lawrence Livermore Laboratory Report, UCRL-52092, 1976.
(24) Heft, R. E., paper presented at the Third International Conference on Nuclear Methods in Environmental and Energy Research, Columbia, Mo., Oct 10-13, 1977.
(25) Murphy, J., *At. Absorpt. Newsl.*, 14, 151 (1975).
(26) Bonner, N. A., Bazan, F., Camp, D. C., *Chem. Instrum.*, 6, 1-36 (1975).
(27) Ondov, J. M., Zoller, W. H., Olmez, K., Aras, N. K., Gordon, G. E., Ranticelli, L. A., Able, K. H., Filby, R. H., Shah, K. R., Ragaini, R. C., *Anal. Chem.*, 47, 1102-9 (1975).
(28) Ondov, J. M., Ragaini, R. C., Heft, R. E., Fisher, G. L., Silberman, D., Prentice, B. A., in Proceedings of the 8th Materials Research Symposium, Methods and Standards for Environmental Measurement, Gaithersburg, Md., Sept 20-24, in press; Lawrence Livermore Laboratory, Preprint UCRL-78194, 1976.
(29) Fisher, G. L., Chang, P. V., Brummer, M., *Science*, 192, 555-6 (1976).
(30) Ulrich, G. D., "An Investigation of the Mechanism of Fly-Ash Formation in Coal-Fired Utility Boilers", Interim Report, US-ERDA FE-2205-1, May 28, 1976.
(31) Padia, A. S., Sarafim, A. I., Howard, J. B., paper presented at the Combustion Institute's Central States Section, April 1976.
(32) Fuch, N. A., "The Mechanics of Aerosols", MacMillan, New York, 1964, pp 21-30.
(33) Gordon, G. E., Zoller, W. H., Gladney, E. S., Proceedings of 2nd International Conference on Nuclear Methods and Environmental Research, Columbia, Mo., 1974, pp 344-53.
(34) Gladney, E. S., Owens, J. W., *J. Environ. Health*, A11(4&5), 297-311 (1976).
(35) Gluskoter, H. J., Ruch, R. R., Miller, W. G., Cahill, R. A., Dreher, G. B., Kuhn, J. K., "Trace Elements in Coal: Occurrence and Distribution", Illinois State Geological Survey, Circular 499, 1977.

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Comparison of Particle Size Distributions and Elemental Partitioning from the Combustion of Pulverized Coal and Residual Fuel Oil

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ABSTRACT

U.S. Environmental Protection Agency (EPA) research examining the characteristics of primary PM generated by the combustion of fossil fuels is being conducted in efforts to help determine mechanisms controlling associated adverse health effects. Transition metals are of particular interest, due to the results of studies that have shown cardiopulmonary damage associated with exposure to these elements and their presence in coal and residual fuel oils. Further, elemental speciation may influence this toxicity, as some species are significantly more water-soluble, and potentially more bio-available, than others. This paper presents results of experimental efforts in which three coals and a residual fuel oil were combusted in three different systems simulating process and utility boilers. Particle size distributions (PSDs) were determined using atmospheric and low-pressure impaction as well as electrical mobility, time-of-flight, and light-scattering techniques. Size-classified PM samples from this study are also being utilized by colleagues for animal instillation experiments.

Experimental results on the mass and compositions of particles between 0.03 and >20 µm in aerodynamic diameter show that PM from the combustion of these fuels produces distinctive bimodal and trimodal PSDs, with a fine mode dominated by vaporization, nucleation, and growth processes. Depending on the fuel and combustion equipment, the coarse mode is composed primarily of unburned carbon char and associated inherent trace elements (fuel oil) and fragments of inorganic (largely calcium-alumino-silicate) fly ash including trace elements (coal). The three coals also produced a central mode between 0.8- and 2.0-µm aerodynamic diameter. However, the origins of these particles are less clear because vapor-to-particle growth processes are unlikely to produce particles this large.

Possible mechanisms include the liberation of micron-scale mineral inclusions during char fragmentation and burnout and indicates that refractory transition metals can contribute to PM <2.5 µm without passing through a vapor phase. When burned most efficiently, the residual fuel oil produces a PSD composed almost exclusively of an ultrafine mode (~0.1 µm). The transition metals associated with these emissions are composed of water-soluble metal sulfates. In contrast, the transition metals associated with coal combustion are not significantly enriched in PM <2.5 µm and are significantly less soluble, likely because of their association with the mineral constituents. These results may have implications regarding health effects associated with exposure to these particles.

IMPLICATIONS

Transition metals are hypothesized to play a significant role in causing adverse health effects associated with exposure to $PM_{2.5}$. The concentration, speciation, and solubility of transition metals in $PM_{2.5}$ generated by the combustion of fossil fuels can depend upon the fuel type and combustor design. The results presented in this paper have implications for policymakers and researchers evaluating possible sources and control of $PM_{2.5}$ containing transition metals.

INTRODUCTION

Fine PM has been of considerable environmental interest in recent years because of a number of research studies correlating short-term exposure of ambient levels of fine PM with acute adverse health effects.[1] These studies were summarized by the U.S. Environmental Protection Agency (EPA)[2,3] and reviewed by EPA's Clean Air Scientific Advisory Committee, which concluded that there was evidence linking ambient fine PM concentrations and adverse health effects.[4] These studies were the basis for a revision of the National Ambient Air Quality Standards for PM that included a standard for PM <2.5 µm in diameter ($PM_{2.5}$).[5]

In the ambient atmosphere, fine PM is composed primarily of sulfates, nitrates, condensed organics, carbonaceous soot, and inorganic aerosols, formed during high-temperature processes such as the combustion of fuels containing trace quantities of metals and other impurities.[2,6,7] Formation of these small particles is heavily influenced by vaporization, condensation, and other gas-to-particle conversion processes. In contrast, the coarse fraction of PM tends to be composed of particles formed by mechanical (e.g., fragmentation, grinding, crushing, and entrainment) processes. Because they are formed by different mechanisms, the fine and coarse fractions of PM tend to have different compositions. Particle composition has been identified as one of the possible factors driving the adverse health effects associated with exposure to ambient PM.[8]

Health effect researchers have identified at least two aspects of particle composition that appear to exacerbate health damage from particles. The first is related to water-soluble transition metals such as Cu, Fe, Ni, V, and Zn present in the particles.[9–11] The second is aerosol acidity in general. In addition to these composition-related properties, ultrafine particles (those particles <0.1 µm in diameter), regardless of composition, have been identified as potential factors influencing mechanisms for these health impacts.[2] Particles with all of these characteristics (transition metals, acidity, and ultrafine size) are contained in the PM generated from the combustion of fossil fuels such as residual fuel oils and coals. Hence, one might hypothesize fossil-fuel-fired systems to be candidate sources of toxic fine particles that play a significant role in the demonstrated association of adverse health effects with ambient concentrations of fine PM.

The research by Dreher et al.[9–11] has indicated that residual oil fly ash (ROFA) possesses toxic qualities. Unfortunately, the hypothesis that residual oil combustion is the prime source of fine particles causing respiratory distress is not consistent with the currently available epidemiologic data. Residual fuel oils are used in significant quantities in only selected regions of the country. Discounting sales of Bunker C oil, the majority of which is likely to be burned by ships well away from continental coastlines, significant residual oil usage occurs primarily in the northeast and southeast regions of the United States.[12] However, adverse health effects associated with exposure to fine PM are not limited to these regions,[13] suggesting that sources of fine PM other than (or in addition to) those related to residual fuel oil combustion must also be important.

Another source of $PM_{2.5}$ containing transition metals is pulverized coal combustion. Pulverized coal combustion is widespread throughout the United States, and emissions from coal-fired boilers and furnaces account for a much larger fraction of both PM <10 µm in aerodynamic diameter (PM_{10}) and $PM_{2.5}$, compared to residual fuel oil combustion. In 1997, ~165,000 tons of $PM_{2.5}$ was emitted from utility, industrial, commercial, and institutional combustion of coal, compared to 35,000 tons of $PM_{2.5}$ from combustion of residual oil from the same source categories.[14] These values are for primary PM emitted directly from these sources and do not include secondary particles formed from gas-phase precursors such as SO_2 and NO_x. Because both coal and residual fuel oil burned in the United States contain significant levels of transition metals (see Table 1), substantial quantities of these metals are emitted into the atmosphere. In light of the potential health effects associated with inhalation exposure to transition metals, it is worthwhile to explore the formation mechanisms and partitioning of transition metals across different particle sizes for both coals and residual fuel oils.

In a previous study, Miller et al.[15] explored the relationship between residual fuel oil composition, boiler operation, and the physical and chemical characteristics of the PM produced. In a subsequent study, Linak et al.[16] compared the characteristics of PM produced from two types of combustion systems burning the same residual fuel oil. These systems were designed to simulate the operation of small institutional and industrial boilers and large utility boilers. In this study, we compare differences in compositions and particle size distributions (PSDs) of PM from residual fuel oil and coal. Specifically, these tests, conducted at EPA's National Risk Management Research Laboratory in Research Triangle Park, NC, examined the physical and chemical characteristics of PM generated by the combustion of residual fuel oil and coal. A single residual fuel oil was tested in two combustors with significantly different heat transfer characteristics, and three U.S. coals were tested in a single combustor under similar combustion conditions. The purpose of these tests was to examine the relationship between particle size and particle composition, specifically with respect to metal content, for different fossil fuels, and how the relationship may change as fuel or carbon burnout changes. The results of the current and previous studies are intended to form the foundation that may ultimately link measures of acute pulmonary damage to engineering variables.

EXPERIMENTAL

Residual oil experiments were performed in two types of combustion systems. These systems represent extremes of a range of practical conditions under which fuel oil is burned. Although they may not represent specific boilers

Table 1. Fuel analysis.

	Western Kentucky Bituminous	Montana Subbituminous	Utah Bituminous	High Sulfur No. 6 Oil
Proximate Analysis[a] (%)				
Moisture	6.97	11.36	5.97	0.50
Volatile matter	35.86	37.18	38.58	
Fixed carbon	49.66	41.05	45.75	
Ash	7.51	10.41	9.69	0.10
HHV[b], Btu/lb	11291	9526	11289	18270
HHV, kcal/kg	6273	5292	6272	10150
Ultimate Analysis[c] (%)				
C	70.17	64.87	69.23	85.61
H	4.57	3.97	4.87	10.38
N	1.49	1.03	1.45	0.35
S	3.11	0.83	0.96	2.33
O[d]	12.59	17.56	13.18	0.92
Ash	8.07	11.74	10.31	0.10
Trace Elements[c] (μg/g fuel)				
As	4.68	1	2	0.1
Be	1.6	0.4	0.8	<0.3
Cd	<0.2	<0.2	<0.2	0.60
Cl	35.5	28.7	33.9	
Cr	11	4	12	1.05
Cu	3	2.89	3.37	3.5
Fe	9210	2560	2000	21
Pb	3.06	3.42	2.87	4.5
Mg	79.4	1700	1710	
Mn	6.71	62.3	59.9	
Hg	0.15	0.08	0.07	0.10
Mo	3.25	ND	ND	
Ni	6.35	2.39	ND	30
K	81.7	ND	44.6	
Se	2	1	2	<0.1
Na	332	300	409	
V	13	4.55	4.25	220
Zn	30.8	ND	ND	74

Notes: [a]As received (wet); [b]Higher heating value; [c]Dry basis, ND indicates nondetect analysis, empty cells indicate no analysis for this element was attempted; [d]By difference.

in all respects, they were investigated here with a view to determining how this range of combustion conditions influences the characteristics of fine particles and the mechanisms that form them. The first system is a small fire-tube boiler, in which combustion occurs in tubes surrounded by water or steam. These types of small boilers have large heat transfer surfaces, small volumes, relatively short residence times, cold walls, and high gas quenching rates (~500 K/s), and often produce emissions with relatively high carbon contents due to unburned carbonaceous char. The second system is a laboratory-scale refractory-lined combustor designed to simulate the time/temperature environments of larger utility boilers and incinerators. In large utility boilers, the water or steam, rather than the combustion gases, is contained in tubes. These systems, including the refractory-lined combustor, operate at higher temperatures with lower quenching rates (~150 K/sec). As will be discussed later, particle emissions from this system contain very little unburned carbon and better approximate emissions from large oil-fired utility boilers, as reported in the literature.[17,18]

Fire-Tube Boiler

Residual oil experiments were performed using a commercially available, North American, three-pass, fire-tube package boiler. This unit is equipped with a 732-kW North American burner with an air-atomizing oil nozzle. Oil temperature and oil and atomizing air pressures are independently controlled to ensure proper oil atomization. PM samples were extracted at stack locations at temperatures ranging from 450 to 550 K. Additional system details are presented elsewhere.[15]

Refractory-Lined Combustor

Residual oil experiments were also performed using a 59-kW laboratory-scale refractory-lined combustor. This unit is equipped with an International Flame Research Foundation (IFRF) moveable-block variable-air swirl burner, which incorporates an air-atomizing oil nozzle positioned along its center axis and swirling air, which passes through the annulus around the fuel injector to promote flame stability. The burner was configured for a high swirl flame (IFRF Type 2, swirl no. = 1.48) with internal recirculation. Gas and aerosol samples were taken from stack locations at temperatures of ~670 K. All oil experiments (fire-tube boiler and refractory-lined combustor) were performed at a stoichiometric ratio (SR) of 1.2 without secondary air preheat. Additional system details are presented elsewhere.[16]

Pulverized Coal Combustor

Coal combustion experiments were conducted using a down-fired, refractory-lined furnace rated at 50 kW. A schematic of this furnace is presented in Figure 1. In this combustor, pulverized coal is metered from a screw feeder and carried by transport air through a fuel injector into the combustor. Additional axial and tangential airstreams are metered separately into the variable swirl burner and introduced into the combustor as an annular flow around the coal. These flows can be adjusted to create stable flames with the desired degree of swirl. The vertical 4.1 m down-fired combustor is 20-cm inside diameter (ID). At the bottom of the vertical section, the combustion gases make a 90° turn into a 3.7-m-long, 15-cm-ID horizontal sampling

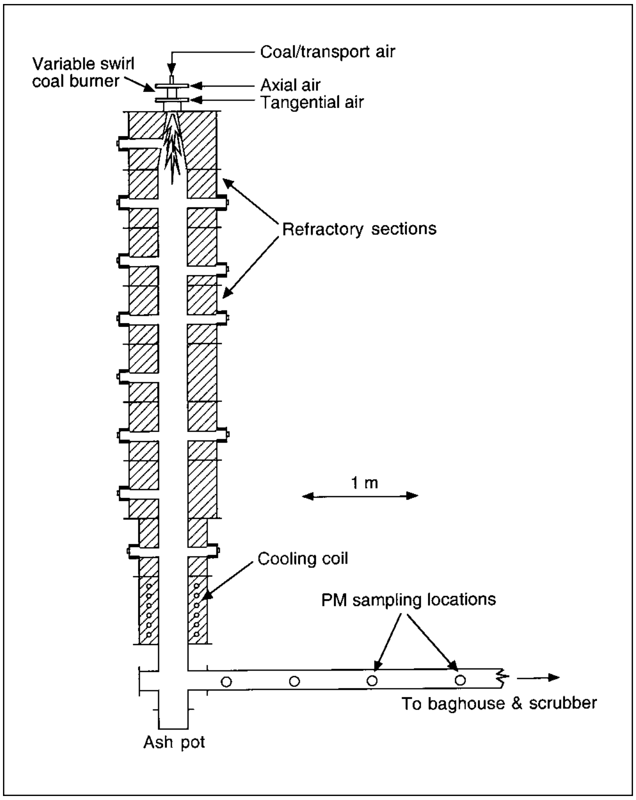

Figure 1. EPA down-fired pulverized coal combustor.

duct. Ports are available along the furnace and exhaust duct for introduction of additional staging air or for introduction of sorbents or extractive sampling. The locations of these ports are shown in Figure 1. Previous test programs burning pulverized coal have resulted in combustion conditions within the furnace similar to those found in full-scale utility units.[19]

Particulate Sampling and Analysis

PM measurements were performed using several methods. Standard EPA Methods 5 and 60 sampling and analytical procedures were used to determine total particulate and metal concentrations using inductively coupled argon plasma atomic emissions spectroscopy (ICP/AES).[20–22] Other metal analyses were determined by X-ray fluorescence (XRF) spectroscopy. Additional samples were analyzed by X-ray absorption fine structure (XAFS) spectroscopy, an element-specific structural analysis that is useful for determining trace element speciation and forms of occurrence in chemically and structurally complex materials such as combustion ash.[23–25]

PSDs were determined by a combination of four techniques used at various times. Instruments based on electrical mobility, time-of-flight, and inertial impaction measurements were used for extracted aerosols; and light-scattering measurements were used for in situ in-stack measurements. Extractive samples were taken for electrical mobility, time-of-flight, and inertial impaction analyses using an isokinetic aerosol sampling system described elsewhere.[26,27] These diluted samples were directed to a TSI Inc. scanning mobility particle sizer (SMPS) and a TSI Inc. aerodynamic particle sizer (APS). The SMPS and APS were configured to yield 54 and 50 channels evenly spaced (logarithmically) over 0.01- to 1.0-µm and 0.5- to 20-µm diameter ranges, respectively. Extracted samples were also directed to three cascade impactors including an Andersen Inc. eight-stage, 28 L/min atmospheric pressure impactor, an MSP Inc. ten-stage, 30 L/min micro-orifice uniform deposit impactor (MOUDI), and a custom-made eleven-stage 28 L/min Berner-type low-pressure impactor.[28] During the oil experiments, in situ light-scattering PSDs were obtained using an Insitec Inc. particle counter sizer velocimeter with a working range of ~0.3–100 µm. Scanning electron microscope (SEM) samples were collected on silver membrane filters to minimize particle charging effects.

In order to collect larger quantities of size-segregated PM for parallel toxicological studies and XAFS analyses, a large dilution sampler capable of sampling 0.28 m^3/min of flue gas was used.[29] The extracted sample passed through a cyclone (50 and 90% collection efficiencies for 1.8- and 2.5-µm-diameter PM, respectively) and was then diluted with clean filtered ambient air (2.8 m^3/min) to approximately ambient temperature (3 sec residence time). The resulting PM was collected on 64.8-cm-diameter Teflon-coated glass fiber filters, transferred to sampling jars, and made available for subsequent chemical, physical, or biological analysis. In addition to the particle sampling and collection devices just described, continuous emission monitors were used to measure stack concentrations of CO, CO_2, NO_x, O_2, and SO_2. These measurements were made in order to monitor and control the combustion environments.

Fly ash samples from the oil experiments and the three coals were subjected to a successive leaching procedure under development to examine the relative solubility of transition metals (Cu, Fe, Ni, V, and Zn) associated with different fly ash matrices. To date, only the dilution sampler filter catches ($PM_{2.5}$) for these four fuels have been examined in this manner. PM samples were placed in successive solutions (30 mL) of distilled water (pH = 7), 0.1 N (equivalent) H_3BO_3 (pH = 5.2 for 0.1 N), 0.1 N CH_3COOH (pH = 2.9), and 0.1 N HCl (pH = 1.1), and sonicated at room temperature for 2 hr. The filtrates and solid residues were separated between successive leaching steps. Finally, these leached samples (and a set of unleached samples) were subjected to a modified Method 3050B extraction procedure to determine total metal content.[30] Briefly, this method uses a 50/50 mixture of HNO_3 and HF, microwaved for 5 min at 340 kPa and 20 min at 550 kPa. After cooling, an additional H_3BO_3 solution is added and microwaved for 10 min at 340 kPa. Solutes were analyzed by ICP/AES.

Experimental Conditions

The no. 6 residual oil used in both oil experimental systems contained 2.33% sulfur and 0.1% ash. Operational characteristics for both systems included similar oil temperatures (380–400 K), atomizing air pressures (200–240 kPa), and stoichiometries (SR = 1.2). The droplet PSD produced using the Delavan Airo Combustion air-atomizing oil nozzle (model 30615-84) in the fire-tube boiler was relatively narrow with a mean diameter between 30 and 40 µm. The refractory-lined combustor experiments used a similar Spraying Systems Co. (model Air Atom 1/4-JSS) air-atomizing oil nozzle and produced PSDs believed to be similar to those for the boiler studies. Therefore, any differences in carbon burnout may be attributed to differences in temperature history rather than in droplet size. Stack O_2 concentrations ranged between 3.4 and 3.6% for all experiments.

Two western U.S. coals (Montana subbituminous and Utah bituminous) and one eastern U.S. coal (western Kentucky bituminous) have been examined. The coals were burned under conditions that simulated as closely as possible those conditions typical of a full-scale utility boiler. Stack O_2 concentrations for the coal combustion tests ranged from 3.5 to 3.8%, with CO values near 60 ppm for the Montana coal and 135 ppm for the western Kentucky and Utah coals. Heat input rates averaged 22.9 kW for the Montana coal, 19.7 kW for the western Kentucky coal, and 20.2 kW for the Utah coal. Average NO_x concentrations for the three coals ranged between 440 and 480 ppm, and SO_2 concentrations averaged 430 ppm for the Montana coal, 1475 ppm for the western Kentucky coal, and 850 ppm for the Utah coal (all values uncorrected for O_2 concentration).

Table 1 presents the proximate, ultimate, and trace element analyses for the three coals and one residual fuel oil examined. Heating values are also included. In contrast to the residual oil, which contained only 0.1% ash, the coal ash contents ranged from 7.5 to 10.4% (as received). However, the residual oil sulfur concentration was almost as high as the western Kentucky coal (2.33 and 3.11%, respectively). The two western coals each had sulfur concentrations less than 1%. Also of note are the high transition metal (Fe, Ni, V, and Zn) concentrations in the residual oil and the high Fe concentrations in the coals. Although not measured and presented here, coals often contain very high concentrations of Al, Ca, and Si. Hardesty and Pohl[31] report ranges of Al, Ca, and Si concentrations in U.S. coals of 0.3–2.3, 0.005–1.2, and 0.5–41%, respectively. Galbreath et al.[24] report Al and Si concentrations in a similar high sulfur no. 6 oil of 19 and 94 ppm, respectively. Walsh et al.[32] report ranges of Al, Ca, and Si concentrations from three medium sulfur residual oils of 21–44, 13–23, and 23–89 ppm, respectively.

RESULTS AND DISCUSSION

PM and Trace Element Emissions

PM mass emissions, emission factors, and trace element emissions for the three coals and two fuel oil conditions are presented in Table 2. Also presented are the mass fractions of $PM_{2.5}$, as well as the weight percent of unburned carbon and loss on ignition (LOI). PM emissions for the three coals and one of the two fuel oil conditions are based on triplicate averages. Standard deviations are included. These data indicate that uncontrolled PM emissions from the three coals ranged between 3800 and 4400 mg/m^3 compared to 90 and 180 mg/m^3 for the fuel oil.

Differences seen between the two fuel oil conditions are likely the result of differences in the heat transfer, time/temperature profiles, and quenching rates characteristic of the two types of combustion equipment used, and are consistent with data published from field measurements.[16] However, even though the uncontrolled PM emissions for the three coals are over 20 times greater than those for the oil experiments, Table 2 indicates that the mass fraction of $PM_{2.5}$ for the coals is very much smaller (4.3–6.7%) compared with the oil (40–100%). This is likely due to differences in the chemical and physical nature in which inorganic elements are bound within the two types of fossil fuels. Unburned carbon and LOI values for the two bituminous coals (western Kentucky and Utah) were ~10–11 and 13–14%, respectively. While somewhat high, these values are reasonable for small research coal combustors and not too unusual even for full-scale utility boilers. Lower unburned carbon (0.5%) and LOI (2.3%) are seen for the Montana subbituminous coal and are characteristic of the behavior of lower rank coals. LOI values for the two oil conditions are very different (90 and 0%), and this behavior, again, is likely the result of differences in the heat transfer characteristics between the fire-tube boiler and refractory-lined combustor. Table 2 also indicates that, in general, coal has significantly higher trace element emissions compared with oil (uncontrolled). However, notable exceptions exist, including emissions of V, Zn, and Ni, which are 8–24 times higher from residual oil combustion compared with coal combustion.

Table 3 presents size-classified trace element concentrations as well as weight percents of unburned carbon and LOI in PM less than and greater than ~2.5 µm aerodynamic diameter. These analyses were made from the cyclone and filter catches from the dilution sampling system used to collect large quantities of PM. The data indicate that the fine PM fraction tends to be enriched in many of these trace elements compared with the coarse PM fraction, and

Table 2. PM and trace element emissions and emission rates.[a]

	Western Kentucky	Montana	Utah	High Sulfur No. 6 Oil Fire-Tube Boiler	High Sulfur No. 6 Oil Refractory-Lined Combustor
Total Emissions					
PM emissions[b] (mg/m^3) standard dev.	3807 (564)	4374 (246)	4323 (374)	184 (6)	93
PM mass fraction[c] <2.5 μm	0.043	0.050	0.067	0.395	~1
PM emission factor (lb/10^6 Btu) (kg/10^6 J)	3.00 1.44e-3	3.30 1.58e-3	3.32 1.59e-3	0.123 5.29e-5	0.052 2.50e-5
Unburned carbon[d] (wt %)	10.2	0.5	10.9		
LOI[4] (wt %)	12.9	2.3	14.5	89.9	~0
Trace Element Emissions (mg/m^3)					
Sb	0.41	0.05		0.0077	
As	0.76	0.41	0.24	0.0063	
Be	0.08	0.03		0.00009	
Cd	0.04	0.01	0.003	0.0035	
Cr	0.57	0.26	0.35	0.011	
Cu	0.33	0.40	0.30	0.170	0.200
Fe	504.75	84.87	92.98	0.740	1.200
Pb	0.11	0.27	0.06	0.089	
Mg	5.83	46.52		1.200	1.700
Mn	0.46	5.23		0.016	
Hg				<0.0022	
Ni	0.48	0.17	0.21	1.200	1.400
Na					2.100
V	1.62	0.48	0.58	9.800	12.000
Zn	2.61	0.30	0.54	3.300	3.000

Notes: [a]Dry basis, concentrations corrected to standard conditions (1 atm, 293 K); [b]PM emissions for four of the five experimental conditions are based on the average of three replicate measurements, standard deviation in parentheses; [c]Based on average mass loadings determined by cascade impactors; [d]Total PM unburned carbon and LOI values are based on the sum of weighted values determined from the dilution sampler filter and cyclone catches (see Table 3).

this enrichment seems to be more pronounced for the oil combustion experiments. In fact, it is noted that essentially all the PM for the refractory-lined combustor oil experiments was <2.5 μm in aerodynamic diameter.

Table 2 presents a comparison of the trace element emissions for the fire-tube boiler and refractory-lined combustor oil experiments. As expected, these concentrations are similar because both systems fired the same high sulfur no. 6 fuel oil. However, in contrast to the PM from the boiler, which exhibited high values for LOI ranging from 60 to 85%, blank-corrected results of filter samples from the combustor tests indicate no mass lost on ignition. The sum of the concentrations of the seven analyzed elements listed in Table 2 for the refractory-lined combustor experiments (last column) account for 21.6 mg/m^3 or ~23% of the total mass emissions. However, if these elements are assumed to exist as sulfates, they then account for 67.1 mg/m^3 or ~72% of the total mass emissions. In fact, XAFS spectroscopy indicated that, while a large portion (40–60%) of the sulfur measured in the fire-tube boiler PM existed as unoxidized organic sulfur (predominantly thiophenic sulfur), essentially all (99%) of the particulate-bound sulfur in the refractory-lined combustor samples was in the form of sulfates.

Emission Factors

The measured mass concentration of 93 mg/m^3 determined from the refractory-lined combustor oil experiments can be converted into an emission factor of ~10.5 lb/10^3 gal. This value is comparable to the emission factor of 9.2 lb/10^3 gal for no. 6 residual oil-fired boilers larger than 100 × 10^6 Btu/hr published in AP-42.[33] This comparison lends further support to the hypothesis that the refractory-lined combustor adequately simulates the combustion environment of larger industrial and utility boilers. As reported by Miller et al.,[15] the range of emission factors determined for the fire-tube boiler was approximately twice that for oil-fired utility boilers. However, dilution samples for these experiments indicate that only 30–50% of the PM mass emissions had an aerodynamic diameter <2.5 μm. Hence, the fine PM emission factor for utility boilers may well be greater than that of fire-tube boilers.

Emissions results from this study can be compared to values from the literature. Goldstein and Siegmund[34,35]

Table 3. Trace element concentrations in emitted PM size fractions.[a,b]

	Western Kentucky		Montana		Utah		High Sulfur No. 6 Oil Fire-Tube Boiler		High Sulfur No. 6 Oil Refractory-Lined Combustor	
Trace Element Concentration in Ash Fraction (μg/g)	**<2.5 μm**	**>2.5 μm**	**<2.5 μm**	**>2.5 μm**	**<2.5 μm**	**>2.5 μm**	**<2.5 μm**	**>2.5 μm**	**<2.5 μm**	**>2.5 μm**
Sb							48.6	8.20		
As	132	68.4	62.7	45.3	89.0	59.6	35.9	8.60		
Be							0.46	0.15		
Cd	8.7	3.3	<1.0	<1.0	<1.0	<1.0	19.3	1.84		
Cr	132	108	17.5	19.6	110	78.7	60.2	41.3		
Cu	73.5	51.9	96.7	55.6	95.8	51.5	1050	222	2346	0[c]
Fe	76500	88300	4000	3810	16000	14400	3850	2300	13993	0
Pb	34.5	16.1	93.2	48.4	40.2	<12.3	990	94.2		
Mg							6190	2220	19989	0
Mn							73.2	42.8		
Ni	110	86.2	41.5	29.3	109	39.4	8020	2270	16518	0
S (wt %)	1.12	0.46	0.74	0.01	0.68	0.27			3.2	0
V	356	330	111	84.9	186	123	58900	19900	135718	0
Zn	548	265	141	31.9	144	40.3	21000	2740	34245	0
Unburned carbon (wt %)	11.25	8.83	0.43	0.53	12.86	9.89				
LOI (wt %)	14.96	9.96	1.69	2.79	15.68	13.98	86.6	96.9	~0	0

Notes: [a]Dry basis, empty cells indicate no analysis for this element was attempted; [b]<2.5- and >2.5-μm concentrations are determined from size-classified fly ash from the dilution sampler filter and cyclone catches, respectively; [c]No material was recovered from the cyclone catch for this condition, <2.5-μm elemental concentrations were determined from M-29 samples.

examined the effect of fuel type and combustion modifications on PM emissions from a small 37-kW (50-hp) fire-tube boiler. They report similar PM emissions of ~180 mg/m^3 with carbon contents of up to 80% while burning a similar 2.2% sulfur no. 6 fuel oil. They also noted that efforts to increase PM burnout shift the PSD toward the submicron range. Conversely, Cheng et al.[17] and Bacci et al.[18] examined PM emissions from 30-MW (1 × 10^8 Btu/hr) and 320-MW (1 × 10^9 Btu/hr) fuel-oil-fired power plants, respectively. PM emissions from these units were reported to be 87 mg/m^3 and 40–50 mg/m^3, respectively, even though the 30-MW unit was equipped with a multicyclone PM control system.

The uncontrolled measured mass concentrations for the three coals can be converted to emission factors ranging from 1.4 × 10^{-3} to 1.6 × 10^{-3} kg/10^6 J (3.0–3.3 lb/10^6 Btu). Like the oil experiments, these values are also comparable to emission factors determined for these coals. AP-42[33] estimates that filterable PM emission factors for these pulverized coals from dry-bottom wall-fired and dry-bottom tangentially fired utility boilers would range from 3.3 to 5.5 lb/10^6 Btu. This agreement is remarkable considering the difference in the scales of these units. It is important to note, however, that most utility boilers are equipped with PM control systems and that actual PM emissions from these units are dependent on particle size and the control technology used.

McElroy et al.[36] present particle collection efficiencies for two coal-fired units equipped with a fabric filter baghouse and an electrostatic precipitator, respectively. Their measurements indicate the baghouse produced PM collection efficiencies of >99% over the entire range of particle diameters examined (0.02–10 μm). However, PM collection efficiencies for the electrostatic precipitator were >90% for most particle diameters, and between 80 and 90% for particles between 0.1 and 0.3 μm diameter. This characteristic minimum in particle collection efficiency is typical for particles between 0.1- and 1.0-μm diameter and was also seen in the baghouse data to a lesser extent. Particles in this size range contain neither the mass (momentum) to be removed by impaction nor the high diffusion velocities necessary to migrate to collection surfaces. While most large utility boilers have some kind of PM control, smaller industrial and institutional boilers (often burning residual fuel oils) are much less likely to have such controls. Additionally, these small boilers are often located within urban airsheds.

PSDs

Figure 2 presents representative particle volume distributions for the three coals and oil combustion in the fire-tube boiler (open circles) and refractory-lined combustor (shaded circles). The inset shows more detail in the ultrafine particle size range below 0.1 μm. Together, these

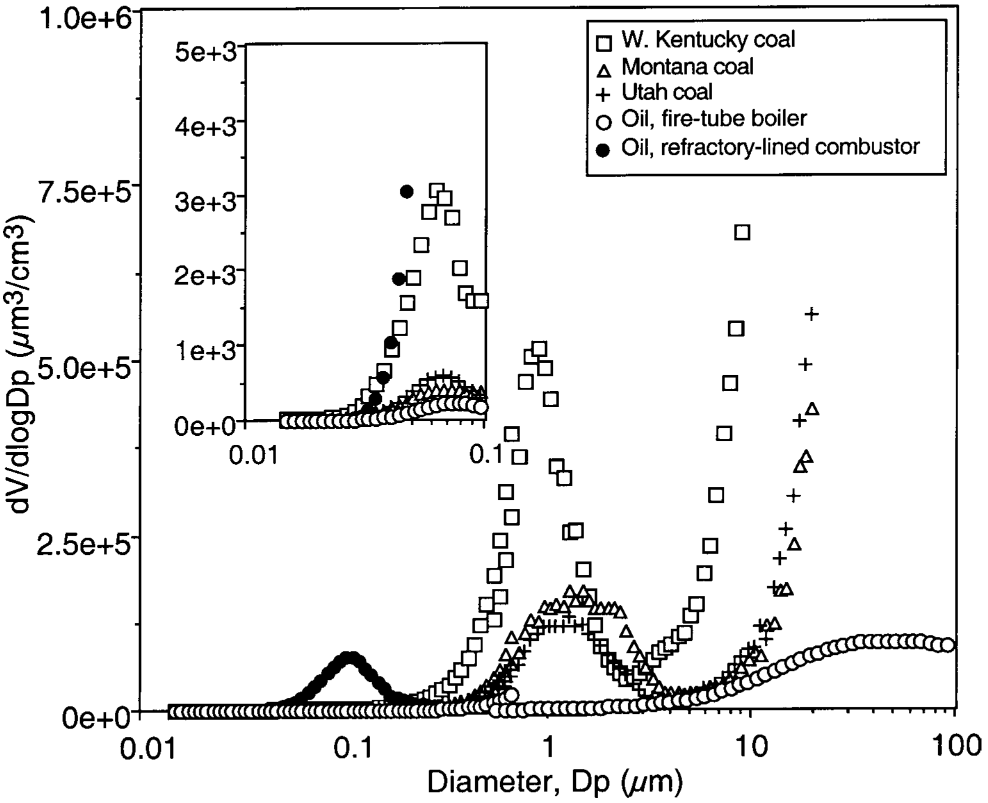

Figure 2. Measured volume PSDs. PSDs between ~0.01 and 1.0 µm diameter were determined by electrical mobility measurements. PSDs greater than ~0.5 µm diameter were determined by light-scattering and time-of-flight measurements.

electrical mobility, time-of-flight, and light-scattering measurements span four decades of particle diameter (0.01–100 µm). The fire-tube boiler and refractory-lined combustor oil PSDs are the same data as plotted in Miller et al.[15] and Linak et al.,[16] respectively. The fire-tube boiler PSDs indicate that most of the particle volume is associated with large (coarse mode) particles >10 µm diameter. The open circle symbols in the inset show that even the fire-tube boiler produces a small accumulation mode with a mean diameter of between 0.07 and 0.08 µm, but that this accumulation mode is much smaller than that for the refractory-lined furnace (shaded circles). Thus, both configurations produced an ultrafine mode, but only the fire-tube boiler produced a bimodal PSD with a very large and dominant coarse mode.

In contrast, the three coals each produce trimodal PSDs. These include small accumulation modes between 0.07 and 0.08 µm, large coarse modes from 7 to 10 µm, and a central mode between 0.8 and 2.0 µm. Unlike the in situ light-scattering technique used during the oil tests, the APS used during the coal combustion experiments does not extend beyond 20 µm. While the accumulation and coarse modes can be described by mechanisms of trace element vaporization, nucleation, and particle growth and residual ash fragmentation, respectively, the mechanisms that produce the central mode are less clear. Model predictions[6,7,16] indicate that coagulation of nucleated vapor cannot produce particles as large as 1-µm diameter. These particles are more likely the result of mineral inclusions that are liberated during the fragmentation and burnout of the coal char particle. This mechanism has been proposed previously to explain supermicron particle formation.[37]

Smith et al.[38] proposed that the presence of cenospheres and plerospheres indicate that a bursting mechanism may be involved. They suggested that gas evolution during rapid heating causes ballooning of some large liquid ash particles. At temperatures slightly higher than that required for cenosphere formation, the viscosity of the liquid particle will be sufficiently small that the particle will burst, releasing a shower of smaller particles. Helble and Sarofim[39] examined the influence of fragmentation on ash PSDs. They measured a mode between 1- and 5-µm diameter which comprised ~25% of the total ash mass and suggest that particles in this size range are formed by perimeter fragmentation of the char during conditions of external diffusion-controlled reaction and excess air.

Baxter[40] also developed a char fragmentation model to predict fly ash PSDs (>0.6 µm diameter) during pulverized coal combustion. Results indicate that the fly ash PSD is sensitive to both the extent and mechanism of fragmentation. For high rank coals, more fly ash particles of ~2- and 15-µm diameter are produced as a result of fragmentation than any other sizes, and predicted PSDs indicate modes at ~2 and 15 µm, which are qualitatively consistent with those presented in Figure 2. The model also predicts that fragmentation is much less important for lignite fuels. Previous reports of trimodal PSDs for coal fly ash are somewhat limited, and may be a consequence of limited ranges of particle diameters examined, improved resolution of current instrumentation, and field data taken downstream of PM control devices, which are very effective in controlling larger particles. McElroy et al.[36] present composite impactor PSDs from a small 25-MW coal-fired boiler. Their PSDs indicate modes at ~0.08-, 2-, and >10-µm diameter comparable to those presented in Figure 2. More recently, Seames and Wendt[41] have also seen evidence of trimodal PSDs during combustion of an Illinois no. 6 bituminous coal in an uncontrolled laboratory-scale combustor using a low-pressure impactor.

The bimodal PSDs seen for the oil experiments are consistent with a mechanism of metal vaporization/nucleation/coagulation/condensation and incomplete burnout of residual fuel cenospheres.[15,16] SEM images of oil char collected from the fire-tube boiler showed a sponge-like morphology that clearly suggests swelling and extensive pore formation. In general, the extent of ash (metal) vaporization is dependent on carbon burnout. For incomplete combustion, a substantial fraction of the trace metals remain trapped in the unburned char particles, and never escape into the vapor phase. However, as the combustion gases cool, those metals that have vaporized will condense on existing surfaces or, if supersaturation partial pressures are large enough, will nucleate to form new particles. The distinctive submicron peak (between 0.07- and 0.08-µm diameter) is clearly indicative of particles formed by nucleation, coagulation, and condensation of materials that have vaporized. Thus, when large portions of the metal constituents fail to vaporize (open circles), the accumulation mode will be much smaller than when they do vaporize (shaded circles).

The refractory-lined combustor volume PSD (shaded circles) consists exclusively of a narrow submicron accumulation mode with a mean diameter of ~0.1 µm, and both light-scattering measurements and the lack of any cyclone catch containing gray or black particles with measurable LOI support this. Clearly, as the oil char is consumed, the metals have vaporized almost completely and have subsequently nucleated and grown to form the distinctive accumulation mode shown in Figure 2. Comparison between the areas under the submicron volume PSD for the two types of equipment suggests that, while only a very small fraction (<1%) of the metal trace elements are vaporized in the fire-tube boiler, well over 99% of these constituents vaporize in the refractory-lined combustor.

In contrast to residual oils whose ash is almost exclusively bound inherently within the organic molecular structure, very little coal ash is inherently bound. Rather, large fractions of ash components in coal are present as mineral inclusions within the coal particles or as excluded materials, either liberated inclusions during the grinding process or extraneous material collected during mining.[6] As a result, the nature and behavior of coal ash is very different compared with oil. Coal refractory elements, including Al, Ca, and Si, are not easily vaporized and can act to bind otherwise volatile species. Typically, large fractions of coal ash remain in the coarse size fractions with only very small amounts (<1%) vaporizing to produce the accumulation mode. However, the central mode near 1-µm diameter (see Figure 2) indicates that fine PM (including transition metals) may be produced from coal combustion by mechanisms other than vaporization. Interactions between alkali metals and Al- and Si-containing species in coal have been studied by Gallagher et al.,[42] who examined such processes for Na and K with implications for understanding and controlling boiler fouling processes. Additionally, several studies have purposely introduced Al-, Ca-, and Si-based compounds to adsorb toxic trace elements, including Pb and Cd, in waste incineration processes.[26,43,44]

Figure 3 presents mass distribution data for the three coals determined by gravimetric analysis of in-stack and extractive low-pressure cascade impactors. While not as resolved or sensitive as the electronic measurements presented in Figure 2, these data indicate the same qualitative information, including a large coarse mode from 8 to 10 µm and a central mode between 1 and 5 µm. Figure 4 presents the elemental mass fraction distributions of several selected transition metals determined by XRF analysis from a set of MOUDI samples for the western Kentucky coal. These mass fraction data have been normalized by dlogDp to correct for differences in cut-off diameters that might otherwise skew the distribution. However, as a result of this normalization, the data from the first (>10 µm) and last stages (<0.056 µm) are lost. Figure 4 indicates that the trace element mass fraction distributions have the same qualitative behavior as the western Kentucky volume distribution presented in Figure 2; that is, a small accumulation mode ~0.1 µm and a central mode ~1 µm. The data also indicate that transition metals comprise a portion of the fine PM produced during coal combustion. These elemental PSDs (Figure 4) are also qualitatively similar to those presented by Kauppinen and Pakkanen[45] from a utility-scale pulverized coal boiler burning a Polish

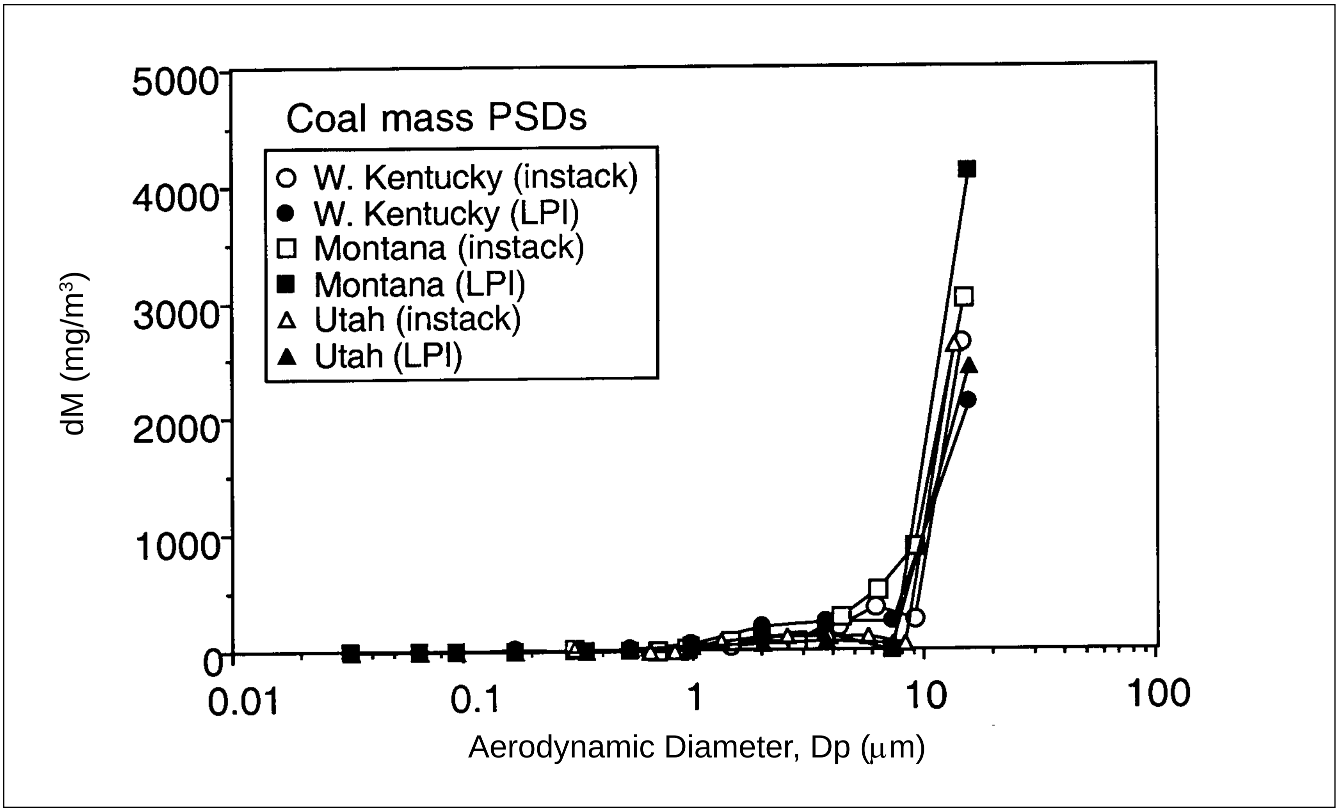

Figure 3. Measured coal mass PSDs.

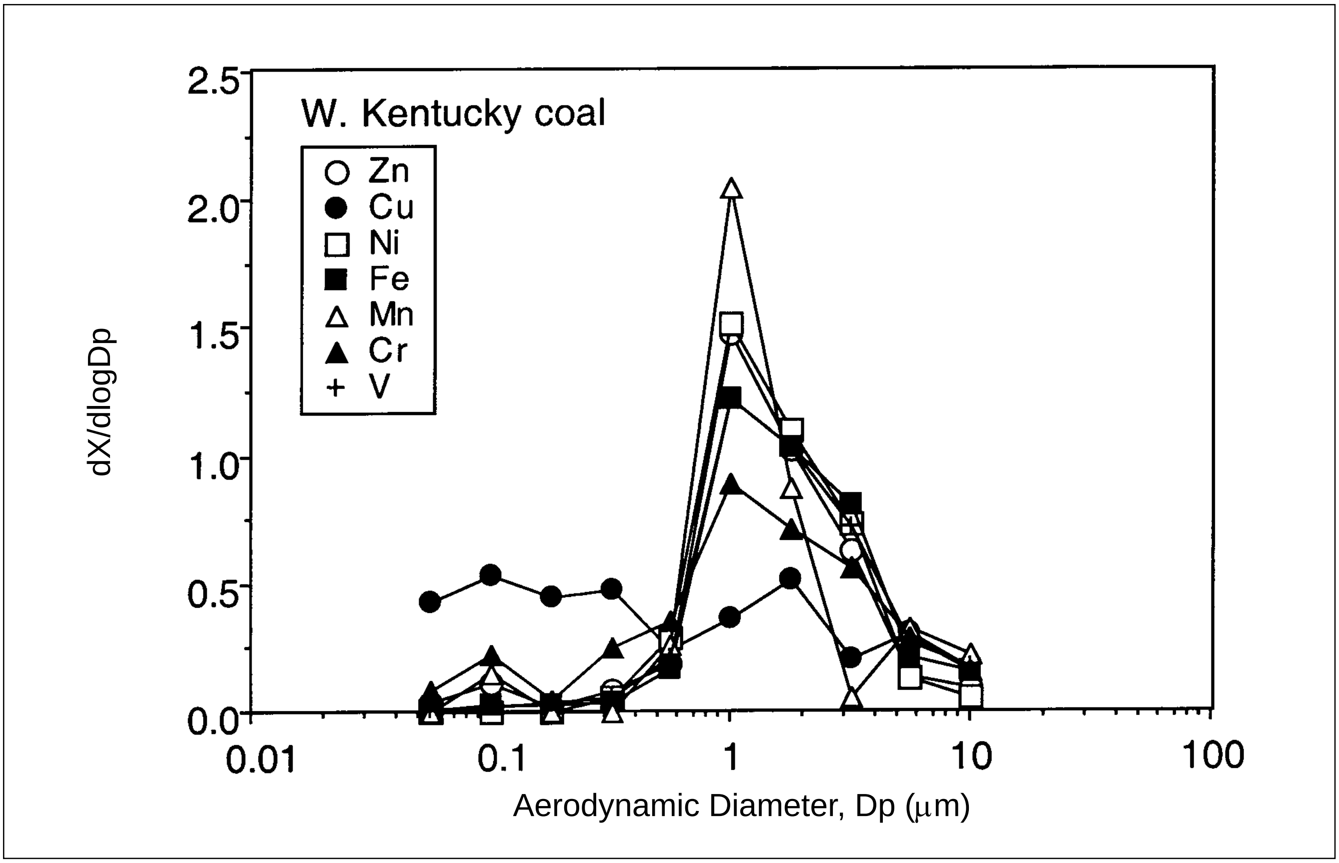

Figure 4. Elemental PSDs for the western Kentucky coal.

coal. Their measurements, taken downstream of the electrostatic precipitator, indicate total mass emissions of 24.3 mg/Nm^3, of which 1.2 mg/Nm^3 (~5%) was comprised of the transition metals Zn, Cu, Ni, Fe, Mn, and V (Cr was not measured).

Successive Leaching

Based on the hypothesis that soluble forms of transition metals may play important roles in the mechanisms resulting in adverse health effects, research was initiated to examine and compare the relative solubility of these elements from different fly ash matrices. This approach, based on a procedure of successively leaching fly ash samples with acids of increasing strength, was briefly described earlier and remains under development. The intent is to compare the relative solubility of these metals from different ash matrices to various health effect end points determined for the same ash samples by colleagues within EPA's National Health and Environmental Effects Research Laboratory. Figure 5 presents results comparing the relative solubility of five transition metals from the $PM_{2.5}$ fraction of fly ash samples from the residual fuel oil and the three coals examined to date. Note, however, that the residual fuel oil fly ash used for these analyses was collected from a third in-house liquid fuel combustor designed to simulate a water-wall package boiler. These samples were collected during a test campaign to examine the combustion characteristics of an Orimulsion fuel and compare its emissions to those of a residual fuel oil.[46] Nonetheless, the package boiler simulator produced fly ash with 38% LOI. This value is higher than that for the refractory-lined combustor, but notably lower than that of the fire-tube boiler (see Table 2), and is consistent with the moderate heat transfer and quench rates associated with this boiler design.

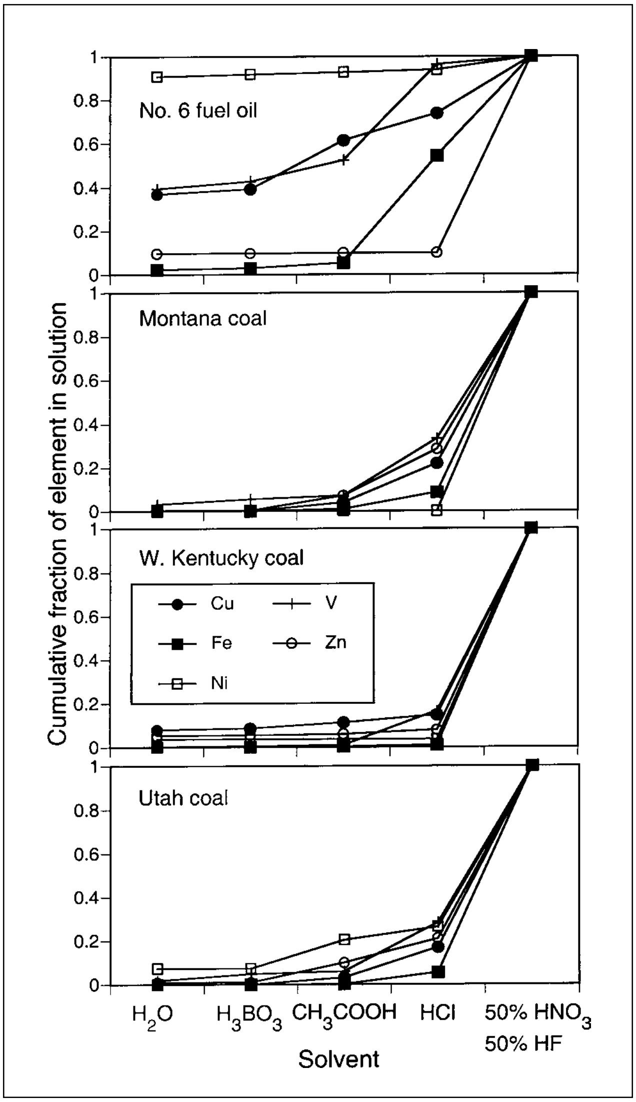

Figure 5. Elemental solubility by successive leaching of $PM_{2.5}$ fly ash.

Figure 5 indicates that several of the transition metals associated with the $PM_{2.5}$ ROFA are readily soluble even in water, but these same metals are relatively insoluble from each of the three $PM_{2.5}$ coal fly ash samples. The data indicate that, compared to the oil fly ash sample, strong acids are necessary to dissociate these metals from the coal fly ash. Another interesting result seen in Figure 5 is that not all of the transition metals have similar solubilities in each of the acids. The residual oil data show Ni is almost completely soluble in water, while V and Cu are partially soluble and Zn and Fe are only minimally soluble. Stronger acids are necessary to dissolve these elements. This may be related to the nature of the trace element speciation with the fly ash and may influence the potential bioavailability of the transition metal. The relative insolubility of these metals from the coal fly ashes is likely the result of the mineral nature of coal ash and large quantities of Si, Al, and Ca that are known to interact with trace metals to form relatively insoluble alumina, silica, and calcium complexes. It should be re-emphasized that this leaching process is only intended to determine the relative solubility of different trace elements in different ash matrices. It is not intended to simulate any actual in vivo process. Other work has shown that transition metal mobility may be increased by the presence of organic chelating compounds.[47,48]

CONCLUSIONS

Fine particle emissions from residual fuel oil and pulverized coal combustion were examined and compared. A laboratory-scale refractory-lined combustor, which was shown to simulate combustion conditions of a large utility residual oil-fired boiler (as far as particulate emission factors were concerned), produced fly ash particles with an essentially unimodal PSD with a mean diameter of ~0.1 µm. Conversely, a pilot-scale fire-tube package boiler produced particles with a weak bimodal size distribution, which included a small fraction (~0.2%) of the mass with particle diameters below 0.1 µm and a large fraction (~99.8%) of the mass with particle diameters between 0.5 and 100 µm. Here the large particles were shown to consist of large porous carbonaceous cenospheres resulting from poor carbon burnout, a characteristic not uncommon for that class of equipment. Although the total particulate mass concentrations in the flue gas of the refractory-lined combustor were less than half those of the fire-tube boiler, ultrafine particle concentrations of the refractory-lined combustor were notably larger than those measured for the fire-tube boiler. Volume PSDs obtained from two independent particle-sizing instruments were, with only a few very reasonable assumptions, consistent with independently measured total mass emission rates for both equipment types.

Three pulverized coals burned in a laboratory-scale down-fired combustor produced trimodal PSDs. Uncontrolled mass emissions for these coals were over 20 times higher than those for the residual fuel oil. However, most of this mass contributes to a large coarse mode with only 4–7% of this mass associated with $PM_{2.5}$.

The results presented here provide insight into mechanisms of fine particle formation from residual oil and pulverized coal combustion. For the refractory-lined combustor burning residual oil, where very few large particles were formed, the PSD was nearly unimodal with a mean diameter of ~0.1 µm. These particles were composed primarily of trace species containing Cu, Fe, Ni, V, Zn, and S. Additionally, these particles contained very little carbon (based on LOI), and the particulate-bound sulfur was speciated almost exclusively as sulfates. The weak bimodal behavior of the PM generated by residual oil combustion in the fire-tube boiler produced a fine mode (composed predominantly of metals and sulfur) with a mean diameter of ~0.7–0.8 µm, and a broad coarse mode (comprised primarily of char) with a mean diameter of ~40–50 µm. Both of these types of behavior provide circumstantial evidence for a mechanism of fine particle formation from residual oil combustion. Commonly considered nonvolatile metals are likely released into the gas phase during the last stages of carbon burnout, and because of incomplete carbon burnout, the accumulation mode for particles formed from vapor nucleation was very small for the fire-tube boiler. For the refractory-lined combustor, where char burnout was nearly complete, most of the nonvolatile metals were released into the gas phase.

For the coal experiments, the unburned carbon and LOI ranged from 0.5 to 11.0% and 2.0 to 15%, respectively. While slightly high, these values are not atypical of many utility-scale boilers. The coal PSDs indicate a small accumulation mode ~0.1-µm diameter and a large coarse mode beginning ~10-µm diameter. Similar to the oil PSDs, these modes are consistent with mechanisms involving gas-to-particle formation and growth and residual inorganic ash remaining after char burnout. However, unlike the oil PSDs, the coal data indicate a third central mode between 0.8- and 2.0-µm diameter. Particles of this size are too large to be the result of gas-to-particle growth processes, and are more likely the consequence of micron-scale mineral inclusions liberated during char fragmentation and burnout. This provides a mechanism for refractory transition metals to contribute to $PM_{2.5}$ without the necessity of passing through a vapor phase.

Successive leaching of the $PM_{2.5}$ fly ash from the different fuels may prove to be a useful technique to provide insight into mechanisms controlling elemental speciation, partitioning, and bioavailability. Preliminary results using five acidic solvents of increasing strengths indicate that five transition metals associated with coal are relatively insoluble in all but the most aggressive acids. Conversely, several of these metals associated with ROFA were readily or partially water-soluble. These results may have important implications in the determination of what particle characteristics play significant roles in causal mechanisms of pulmonary damage associated with exposure to fine PM.

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REFERENCES

1. *Particles in Our Air: Concentrations and Health Effects*; Wilson, R., Spengler, J.D., Eds.; Harvard University Press: Cambridge, MA, 1996.
2. *National Ambient Air Quality Standards for Particulate Matter: Proposed Decision*; 40 CFR, Part 50; U.S. Environmental Protection Agency; U.S. Government Printing Office: Washington, DC, 1996.
3. Bachmann, J.D.; Damberg, R.J.; Caldwell, J.C.; Edwards, C.; Koman, P.D. *Review of the National Ambient Air Quality Standards for Particulate Matter: Policy Assessment of Scientific and Technical Information*; EPA-452/R-96-013 (NTIS PB97-115406); U.S. Environmental Protection Agency; Office of Air Quality Planning and Standards: Research Triangle Park, NC, 1996.
4. Wolff, G.T. *Closure by the Clean Air Scientific Advisory Committee (CASAC) on the Staff Paper for Particulate Matter*; EPA-SAB-CASAC-LTR-96-008; Science Advisory Board: Washington, DC, June 1996.
5. *Fed. Regist.* 62 FR 38652, July 1997.
6. Linak, W.P.; Wendt, J.O.L. Toxic Metal Emissions from Incineration: Mechanisms and Control; *Prog. Energy Combust. Sci.* **1993**, *19*, 145-185.
7. Linak, W.P.; Wendt, J.O.L. Trace Metal Transformation Mechanisms During Coal Combustion; *Fuel Process. Technol.* **1994**, *39*, 173-198.
8. *Review of EPA's Particulate Matter Research Program*; National Research Council; National Academy Press: Washington, DC, 1998.

9. Dreher, K.; Costa, D.; Hoffman, A.; Bonner, J.; Osornio-Vargas, A. Pulmonary Toxicity of Urban Air Particulate Matter (PM). Presented at the A&WMA Meeting on Measurement of Toxic and Related Air Pollutants, Research Triangle Park, NC, May 1996.
10. Dreher, K.; Jaskot, R.; Richards, J.H.; Lehmann, J.R.; Winsett, D.; Hoffman, A.; Costa, D. Acute Pulmonary Toxicity of Size-Fractionated Ambient Air Particulate Matter; *Am. J. Respir. Crit. Care Med.* **1996**, *153(4)*, A15.
11. Dreher, K.; Jaskot, R.; Lehmann, J.R.; Richards, J.H.; McGee, J.K.; Ghio, A.J.; Costa, D.L. Soluble Transition Metals Mediate Residual Oil Fly Ash Induced Lung Injury; *J. Toxicol. Environ. Health* **1997**, *50*, 285-305.
12. *Fuel Oil and Kerosene Sales 1997*; DOE/EIA-0535(97); Energy Information Administration; U.S. Department of Energy: Washington, DC, 1998.
13. Dockery, D.W.; Pope, C.A.; Xu, X.; Spengler, J.D.; Ware, J.H.; Fay, M.E.; Ferris, B.G.; Speizer, F.E. An Association between Air Pollution and Mortality in Six U.S. Cities; *N. Engl. J. Med.* **1993**, *329*, 1753-1759.
14. Nizich, S.V.; Pope, C.A. *National Air Pollutant Emission Trends Update: 1970-1997*; EPA-454/E-98-007; U.S. Environmental Protection Agency; Office of Air Quality Planning and Standards: Research Triangle Park, NC, December 1998.
15. Miller, C.A.; Linak, W.P.; King, C.; Wendt, J.O.L. Fine Particle Emissions from Heavy Fuel Oil Combustion in a Firetube Package Boiler; *Combust. Sci. Technol.* **1998**, *134*, 477-502.
16. Linak, W.P.; Miller, C.A.; Wendt, J.O.L. Fine Particle Emissions from Residual Fuel Oil Combustion: Characterization and Mechanisms of Formation; *Proceeddings of the Combustion Institute;* in press.
17. Cheng, R.J.; Mohnen, V.A.; Shen, T.T.; Current, M.; Hudson, J.B. Characterization of Particulates from Power Plants; *J. Air Pollut. Control Assoc.* **1976**, *26(8)*, 787-790.
18. Bacci, P.; Del Monte, M.; Longhetto, A.; Piano, A.; Prodi, F.; Redaelli, P.; Sabbioni, C.; Ventura, A. Characterization of the Particulate Emission by a Large Oil Fuel Fired Power Plant, *J. Aerosol Sci.* **1983**, *14(4)*, 557-572.
19. Snow, G.C.; Lorrain, J.M. *Evaluation of Innovative Combustion Technology for Simultaneous Control of SO_x and NO_x*; EPA-600/2-87-032 (NTIS PB 87-188926); U.S. Environmental Protection Agency; Air and Energy Engineering Research Laboratory: Research Triangle Park, NC, 1987.
20. Garg, S. EPA Method 0060–Methodology for the Determination of Metals Emissions in Exhaust Gases from Hazardous Waste Incineration and Similar Combustion Processes. In *Methods Manual for Compliance with the BIF Regulations: Burning Hazardous Waste in Boilers and Industrial Furnaces*; EPA/530-SW-91-010 (NTIS PB91-120006); U.S. Environmental Protection Agency; Office of Solid Waste and Emergency Response: Washington, DC, 1990; pp 3-1 to 3-48.
21. *U.S. EPA Test Method 1A-Sample and Velocity Traverses for Stationary Sources with Small Stacks or Ducts*; 40 CFR Part 60, Appendix A; Government Institutes Inc.: Rockville, MD, 1994.
22. *U.S. EPA Test Method 5–Determination of Particulate Emissions from Stationary Sources*; 40 CFR Part 60, Appendix A; Government Institutes Inc.: Rockville, MD, 1994.
23. Galbreath, K.C.; Zygarlicke, C.J.; Huggins, F.E.; Huffman, G.P.; Wong, J.L. Chemical Speciation of Nickel in Residual Oil Ash; *Energy Fuels* **1998**, *12*, 818-822.
24. Galbreath, K.C.; Zygarlicke, C.J.; Toman, D.L.; Huggins, F.E.; Huffman, G.P. Nickel and Chromium Speciation of Residual Oil Combustion Ash; *Combust. Sci. Technol.* **1998**, *134*, 243-262.
25. Huggins, F.E.; Huffman, G.P.; Robinson, J.D. Speciation of Elements in NIST Particulate Matter SRMs 1648 and 1650; *J. Hazard. Mater.* **2000**, *74*, 1-23.
26. Scotto, M.A.; Peterson, T.W.; Wendt, J.O.L. Hazardous Waste Incineration: The In Situ Capture of Lead by Sorbents in a Laboratory Down-Flow Combustor; *Proceedings of the Combustion Institute;* **1992**, *24*, 1109-1118.
27. Linak, W.P.; Srivastava, R.K.; Wendt, J.O.L. Metal Aerosol Formation in a Laboratory Swirl Flame Incinerator; *Combust. Sci. Technol.* **1994**, *101(1-6)*, 7-27.
28. Hillamo, R.E.; Kauppinen, E.I. On the Performance of the Berner Low Pressure Impactor; *Aerosol Sci. Technol.* **1993**, *14*, 33-47.
29. Steele, W.J.; Williamson, A.D.; McCain, J.D. *Construction and Operation of a 10 cfm Sampling System with a 10:1 Dilution Ratio for Measuring Condensable Emissions*; EPA/600-8-88-069 (NTIS PB88-198551); U.S. Environmental Protection Agency; Air and Energy Engineering Research Laboratory: Research Triangle Park, NC, 1988.
30. U.S. EPA Test Method 3050B. In *Test Methods for Evaluating Solid Waste*; EPA-SW-846; U.S. Environmental Protection Agency: Washington, DC, December 1996; Vol 1A. CD-ROM Version 3, Revision 2, http://www.epa.gov/epaoswer/hazwaste/test/3xxx.htm.
31. Hardesty, D.R.; Pohl, J.H. *The Combustion of Pulverized Coals–An Assessment of Research Needs*; National Bureau of Standards Special Publication No. 561; National Bureau of Standards: Washington, DC, 1979; pp 1407-1415.
32. Walsh, P.M.; Rovesti, W.C.; Fangmeier, B.A.; Markoja, R.L.; Brown, J.P.; Hopkins, K.C.; Lange, H.B.; Freeman, R.F.; Olen, K.R.; Washington, K.T.; Partick, S.T.; Campbell, G.L.; Harper, D.S.; Teetz, R.D.; Bennett, T.E.; Moore, S.P. Size Distribution of Metals in Particulate Matter Formed During Combustion of Residual Fuel Oil. In *Proceedings of the Electric Power Research Institute 1993 Fuel Oil Utilization Workshop*; EPRI TR-103990, Section 3; Electric Power Research Institute: Palo Alto, CA, 1994; pp 132-149.
33. *Compilation of Air Pollutant Emission Factors*; Vol. 2: Stationary Point and Area Sources, 5th ed.; AP-42; U.S. Environmental Protection Agency; Office of Air Quality Planning and Standards: Research Triangle Park, NC, November 1996.
34. Goldstein H.L.; Siegmund, C.W. Influence of Heavy Fuel Oil Composition and Boiler Combustion Conditions on Particulate Emissions; *Environ. Sci. Technol.* **1976**, *10(12)*, 1109-1114.
35. Goldstein H.L.; Siegmund, C.W. Particle Emissions from Residual Fuel Fired Boilers: Influence of Combustion Modifications; *J. Eng. Power* **1977**, 371-377.
36. McElroy, M.W.; Carr, R.C.; Ensor, D.S.; Markowski, G.R. Size Distribution of Fine Particles from Coal Combustion; *Science* **1982**, *215(4528)*, 13-19.
37. Flagan, R.C.; Friedlander, S.K. Particle Formation in Pulverized Coal Combustion–A Review. In *Recent Developments in Aerosol Science*; Shaw, D.T., Ed.; John Wiley & Sons: New York, 1978; pp 25-57.
38. Smith, R.D.; Campbell, J.A.; Nielson, K.K. Characterization and Formation of Submicron Particles in Coal-Fired Plants; *Atmos. Environ.* **1979**, *13*, 607-617.
39. Helble, J.J.; Sarofim, A.F. Influence of Char Fragmentation on Ash Particle Size Distributions; *Combust. Flame* **1989**, *76*, 183-196.
40. Baxter, L.L. Char Fragmentation and Fly Ash Formation During Pulverized-Coal Combustion; *Combust. Flame* **1992**, *90*, 174-184.
41. Seames, W.S.; Wendt, J.O.L. Partitioning of Arsenic, Selenium, and Cadmium during the Combustion of Pittsburgh and Illinois #6 Coals in a Self-Sustained Combustor; *Fuel Process. Technol.*, in press.
42. Gallagher, N.B.; Peterson, T.W.; Wendt, J.O.L. Sodium Partitioning in a Pulverized Coal Combustion Environment; *Proceedings of the Combustion Institute,* **1996**, *26*, 3197-3204.
43. Linak, W.P.; Srivastava, R.K.; Wendt, J.O.L. Sorbent Capture of Nickel, Lead, and Cadmium in a Laboratory, Swirl Flame Incinerator; *Combust. Flame* **1995**, *100*, 241-250.
44. Davis, S.B; Wendt, J.O.L. Mechanism and Kinetics of Lead Capture by Kaolinite in a Downflow Combustor; *Proceedings of the Combustion Institute,* in press.
45. Kauppinen, E.I.; Pakkanen, T.A. Coal Combustion Aerosols: A Field Study; *Environ. Sci. Technol.* **1990**, *12*, 1811-1818.
46. Miller, C.A.; Linak, W.P. The Influence of Carbon Burnout on Submicron Particle Formation from Emulsified Fuel Oil Combustion; *Fuel*, submitted for publication, 2000.
47. Ghio, A.J.; Stonehuerner, J.; Pritchard, R.J.; Piantadosi, C.A.; Quigley, D.R.; Dreher, K.L.; Costa, D.L. Humic-Like Substances in Air Pollution Particles Correlate with Concentrations of Transition Metals and Oxidant Generation; *Inhalation Toxicol.* **1996**, *8*, 479-494.
48. Smith, K.R.; Veranth, J.M.; Lighty, J.S.; Aust, A.E. Mobilization of Iron from Coal Fly Ash Was Dependent Upon the Particle Size and the Source of Coal; *Chem. Res. Toxicol.* **1998**, *11*, 1494-1500.

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Volume 2. Appendices

Appendix A - Median Emission Factors, Determined from Test Report Data, and Total 1990, 1994, and 2010 Emissions, Projected with the Emission Factor Program

Table A-1. Median Emission Factors, Determined from Test Report Data, and Total 1990 and Total 2010 HAP Emissions, Projected with the Emission Factor Program for Inorganic HAPs from Coal-fired Units

Coal-fired units: inorganic HAPs	Estimated total 1990 emissions (tons)	Estimated total 1994 emissions (tons)	Estimated total 2010 emissions (tons)
Antimony	**7.95**	**7.98**	**9.93**
Arsenic	**60.93**	**55.81**	**70.61**
Beryllium	**7.13**	**7.93**	**8.20**
Hydrogen chloride	**143,000**	**134,000**	**155,000**
Hydrogen cyanide (HCN) [a]	**240.66**	**250.8**	**318.31**
Hydrogen fluoride	**19,500**	**23,100**	**25,700**
Cadmium	**3.33**	**3.15**	**3.82**
Chromium	**73.27**	**61.60**	**87.43**
Cobalt	**21.21**	**22.67**	**27.08**
Lead	**75.47**	**61.77**	**86.89**
Manganese	**163.97**	**167.72**	**219.02**
Mercury	**45.80**	**51.34**	**59.74**
Nickel	**58.05**	**52.04**	**68.65**
Phosphorus (P) [b]	**270.74**	**331.41**	**358.09**
Selenium	**153.83**	**183.68**	**213.21**

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[a] Nationwide hydrogen cyanide emissions were determined from stack emission factors and not from EMFs.

[b] Nationwide phosphorous emissions were determined from stack emission factors and not from EMFs.

Table A-4. Median Emission Factors, Determined from Test Report Data, and Total 1990, Total 1994 and Total 2010 HAP Emissions, Projected with the Emission Factor Program for Organic HAPs from Coal-fired Units

Coal-fired units: organic HAPs	Number of emission factors (1990)	Median emission factor: lb/trillion Btu (1990)	Computer program: 1990 total tons	Number of emission factors (1994)	Median emission factor: lb/trillion Btu (1994)	Computer program: 1994 total tons	Number of emission factors (2010)	Median emission factor: lb/trillion Btu (2010)	Computer program: 2010 total tons
1,1,2-trichloroethane	**1**	**4.70**	**40.39**	**1**	**4.70**	**42.10**	**1**	**4.70**	**53.43**
2-chloroacetophenone	**3**	**0.29**	**2.50**	**3**	**0.29**	**2.60**	**3**	**0.29**	**3.30**
2,4-dinitrotoulene	**3**	**0.015**	**0.130**	**3**	**0.015**	**0.130**	**3**	**0.015**	**0.180**
Acetaldehyde	**12**	**6.75**	**58.01**	**12**	**4.85**	**43.44**	**12**	**6.75**	**76.74**
Acetophenone	**7**	**0.68**	**5.84**	**8**	**0.91**	**8.15**	**7**	**0.68**	**7.73**
Acrolein	**6**	**3.25**	**27.93**	**7**	**3.3**	**29.56**	**6**	**3.25**	**36.95**
Benzene	**20**	**2.50**	**21.48**	**22**	**2.50**	**22.40**	**20**	**2.50**	**28.42**
Benzyl chloride	**1**	**0.006**	**0.050**	**1**	**0.006**	**0.050**	**1**	**0.006**	**0.060**
Bis(2-ethylhexyl) phthalate	**9**	**4.10**	**35.24**	**9**	**4.10**	**36.73**	**9**	**4.10**	**46.61**
Bromoform	**1**	**6.60**	**56.73**	**1**	**6.60**	**59.11**	**1**	**6.60**	**75.03**
Carbon disulfide	**8**	**4.30**	**36.96**	**9**	**2.90**	**25.97**	**8**	**4.30**	**48.88**
Carbon tetrachloride	**2**	**3.25**	**27.93**	**2**	**3.25**	**29.11**	**2**	**3.25**	**36.95**
Chlorobenzene	**2**	**3.18**	**27.34**	**2**	**3.18**	**28.48**	**2**	**3.18**	**36.15**
Chloroform	**2**	**3.20**	**27.50**	**3**	**3.00**	**26.87**	**2**	**3.20**	**36.38**
Cumene	**1**	**0.29**	**2.50**	**1**	**0.29**	**2.60**	**1**	**0.29**	**3.30**
Dibutyl phthalate	**5**	**2.8**	**24.07**	**4**	**2.55**	**22.84**	**5**	**2.8**	**31.83**
Ethyl benzene	**5**	**0.41**	**3.52**	**6**	**0.41**	**3.63**	**5**	**0.41**	**4.66**
Ethyl chloride	**1**	**2.40**	**20.63**	**1**	**2.40**	**21.49**	**1**	**2.40**	**27.28**
Methyl chloroform	**4**	**3.42**	**29.35**	**4**	**2.10**	**18.81**	**4**	**3.42**	**38.82**

Table A-4. (Continued)

Coal-fired units: organic HAPs	Number of emission factors (1990)	Median emission factor: lb/trillion Btu (1990)	Computer program: 1990 total tons	Number of emission factors (1994)	Median emission factor: lb/trillion Btu (1994)	Computer program: 1994 total tons	Number of emission factors (2010)	Median emission factor: lb/trillion Btu (2010)	Computer program: 2010 total tons
Ethylene dichloride	3	3.10	26.64	3	3.10	27.76	3	3.10	35.24
Formaldehyde	15	4.00	34.38	14	3.25	29.11	15	4.00	45.47
Hexane	2	0.83	7.10	3	1.50	13.43	2	0.83	9.38
Hexachlorobenzene	1	0.08	0.68	1	0.08	0.70	1	0.08	0.90
Isophorone	2	24.0	206.28	2	24.0	214.97	2	24.0	272.83
Methyl bromide	6	0.89	7.65	6	2.245	20.11	6	0.89	10.12
Methyl chloride	3	5.90	50.71	4	5.5	49.27	3	5.90	67.07
Methyl ethyl ketone	6	8.00	68.76	7	5.00	44.78	6	8.00	90.95
Methyl iodine	1	0.40	3.44	2	5.02	44.97	1	0.40	4.54
Methyl isobutyl ketone	3	4.90	42.12	3	4.90	43.89	3	4.90	55.70
Methyl methacrylate	1	1.10	9.45	1	1.10	9.86	1	1.10	12.51
Methyl tert-butyl ether	1	1.40	12.03	1	1.40	12.54	1	1.40	15.92
Methylene chloride	5	13.0	111.8	7	10.0	89.6	5	13.0	147.8
n-nitrosodimethylamine	1	0.68	5.84	1	0.68	6.09	1	0.68	7.73
Naphthalene	11	0.77	6.62	12	0.32	2.87	11	0.77	8.76
m,p-cresol	2	0.675	5.80	2	0.675	6.05	2	0.675	7.68
o-cresol	3	1.7	14.61	3	1.7	15.22	3	1.7	19.33
p-cresol	1	0.95	8.16	1	0.95	8.51	1	0.95	10.80
Perylene	1	0.075	0.65	1	0.075	0.67	1	0.075	0.86
Pentachlorophenol	1	0.008	0.07				1	0.008	0.09
Phenol	10	6.1	52.43	10	6.1	54.64	10	6.1	69.34

Table A-4. (Continued)

Coal-fired units: organic HAPs	**Number of emission factors (1990)**	**Median emission factor: lb/trillion Btu (1990)**	**Computer program: 1990 total tons**	**Number of emission factors (1994)**	**Median emission factor: lb/trillion Btu (1994)**	**Computer program: 1994 total tons**	**Number of emission factors (2010)**	**Median emission factor: lb/trillion Btu (2010)**	**Computer program: 2010 total tons**
Phthalic anhydride	1	4.9	42.12	1	4.9	43.89	1	4.9	55.70
Propionaldehyde	4	10.35	88.96	4	10.35	92.71	4	10.35	117.66
Quinoline	1	0.053	0.45	1	0.053	0.47	1	0.053	0.61
Styrene	7	3.1	26.64	8	2.4	21.49	7	3.1	35.24
Tetrachloroethylene	5	3.1	26.64	5	3.1	27.76	5	3.1	35.24
Toluene	17	3.6	30.94	19	3.3	29.56	17	3.6	40.92
Trans-1,3-dichloropropene	1	4.7	40.39	1	4.7	42.10	1	4.7	53.43
Trichloroethylene	1	3.1	26.64	1	3.1	27.76	1	3.1	35.24
Vinyl acetate	1	0.42	3.61	1	0.42	3.76	1	0.42	4.77
Vinylidene chloride	2	9.7	83.37	1	6.7	59.69	2	9.7	110.28
Xylenes	2	4.65	39.96	4	3.05	27.32	2	4.65	52.87
o-xylenes	5	0.81	6.96	5	0.81	7.26	5	0.81	9.21
m,p-xylenes	8	1.45	12.46	9	1.2	10.75	8	1.45	16.49
Total TEQ for 2,3,7,8-tetra-chlorodibenzo-p-dioxin	17		9.7 x 10^{-5}	17		1.2 x 10^{-4}	17		1.1 x 10^{-4}
2,3,7,8-tetrachlorodi-benzo-p-dioxin	4	1.5 x 10^{-6}	1.3 x 10^{-5}	6	2.6 x 10^{-6}	2.3 x 10^{-5}	4	1.5 x 10^{-6}	1.8 x 10^{-5}
1,2,3,7,8-pentachlorodi-benzo-p-dioxin	3	2.8 x 10^{-6}	2.4 x 10^{-5}	3	2.8 x 10^{-6}	2.5 x 10^{-2}	3	2.8 x 10^{-6}	3.1 x 10^{-5}
1,2,3,4,7,8-hexachlorodi-benzo-p-dioxin	4	5.9 x 10^{-6}	5.1 x 10^{-5}	4	5.9 x 10^{-6}	5.3 x 10^{-5}	4	5.9 x 10^{-6}	6.7 x 10^{-5}
1,2,3,6,7,8-hexachlorodi-benzo-p-dioxin	4	6.6 x 10^{-6}	5.6 x 10^{-5}	4	6.6 x 10^{-6}	5.9 x 10^{-5}	4	6.6 x 10-6	7.5 x 10^{-5}

Table A-4. (Continued)

Coal-fired units: organic HAPs	Number of emission factors (1990)	Median emission factor: lb/trillion Btu (1990)	Computer program: 1990 total tons	Number of emission factors (1994)	Median emission factor: lb/trillion Btu (1994)	Computer program: 1994 total tons	Number of emission factors (2010)	Median emission factor: lb/trillion Btu (2010)	Computer program: 2010 total tons
1,2,3,7,8,9-hexachlorodi-benzo-p-dioxin	**4**	**7.9 x 10^{-6}**	**6.7 x 10^{-5}**	**5**	**4.2 x 10^{-6}**	**3.7 x 10^{-5}**	**4**	**7.9 x 10-6**	**8.9 x 10^{-5}**
1,2,3,4,6,7,8-heptachlorodi-benzo-p-dioxin	**8**	**4.2 x 10^{-6}**	**3.6 x 10^{-5}**	**10**	**7.4 x 10^{-6}**	**6.6 x 10^{-5}**	**8**	**4.2 x 10-6**	**4.7 x 10^{-5}**
Heptachlorodi-benzo-p-dioxin	**6**	**7.6 x 10^{-5}**	**6.5 x 10^{-4}**	**6**	**7.6 x 10^{-6}**	**6.8 x 10^{-4}**	**6**	**7.6 x 10^{-5}**	**8.6 x 10^{-4}**
Hexachlorodi-benzo-p-dioxin	**7**	**2.7 x 10^{-5}**	**2.3 x 10^{-4}**	**7**	**2.7 x 10^{-5}**	**2.4 x 10^{-4}**	**7**	**2.7 x 10^{-5}**	**3.0 x 10^{-4}**
Octachlorodi-benzo-p-dioxin	**10**	**3.6 x 10^{-5}**	**3.1 x 10^{-4}**	**11**	**2.6 x 10^{-5}**	**2.3 x 10^{-4}**	**10**	**3.6 x 10^{-5}**	**4.1 x 10^{-4}**
Pentachlorodi-benzo-p-dioxin	**6**	**8.0 x 10^{-6}**	**6.9 x 10^{-5}**	**6**	**8.0 x 10^{-6}**	**7.1 x 10^{-5}**	**6**	**8.0 x 10-6**	**9.1 x 10^{-5}**
Tetrachlorodi-benzo-p-dioxin	**9**	**8.8 x 10^{-6}**	**6.8 x 10^{-5}**	**9**	**8.8 x 10^{-6}**	**7.1 x 10^{-5}**	**9**	**8.8 x 10-6**	**9.1 x 10^{-5}**
2,3,7,8-tetrachlorodi-benzofuran	**1**	**4.4 x 10^{-6}**	**3.8 x 10^{-5}**	**9**	**4.2 x 10^{-6}**	**3.7 x 10^{-5}**	**1**	**4.4 x 10-6**	**5.0 x 10^{-5}**
1,2,3,7,8-pentachlorodi-benzofuran	**1**	**4.6 x 10^{-6}**	**3.9 x 10^{-5}**	**5**	**4.6 x 10^{-6}**	**4.1 x 10^{-5}**	**1**	**4.6 x 10-6**	**5.2 x 10^{-5}**
2,3,4,7,8-pentachlorodi-benzofuran	**1**	**4.8 x 10^{-6}**	**4.2 x 10^{-5}**	**6**	**7.6 x 10^{-6}**	**6.8 x 10^{-5}**	**1**	**4.8 x 10-6**	**5.5 x 10^{-5}**
1,2,3,4,7,8-hexachlorodi-benzofuran	**1**	**7.9 x 10^{-6}**	**6.8 x 10^{-5}**	**6**	**7.3 x 10^{-6}**	**6.5 x 10^{-5}**	**1**	**7.9 x 10^{-6}**	**8.9 x 10^{-5}**
1,2,3,6,7,8-hexachlorodi-benzofuran	**1**	**4.0 x 10^{-6}**	**3.4 x 10^{-5}**	**8**	**4.0 x 10^{-6}**	**3.6 x 10^{-5}**	**1**	**4.0 x 10^{-6}**	**4.5 x 10^{-5}**
1,2,3,7,8,9-hexachlorodi-benzofuran	**4**	**6.8 x 10^{-6}**	**5.8 x 10^{-5}**	**5**	**6.3 x 10-6**	**5.6 x 10^{-5}**	**4**	**6.8 x 10-6**	**7.7 x 10^{-5}**
2,3,4,6,7,8-hexachlorodi-benzofuran	**5**	**1.2 x 10^{-5}**	**1.0 x 10^{-4}**	**6**	**1.4 x 10^{-5}**	**1.3 x 10^{-4}**	**5**	**1.2 x 10^{-5}**	**1.4 x 10^{-4}**
1,2,3,4,6,7,8-heptachlorodi-benzofuran	**8**	**5.7 x 10^{-6}**	**4.9 x 10^{-5}**	**9**	**7.1 x 10-6**	**6.4 x 10^{-5}**	**8**	**5.7 x 10^{-6}**	**6.5 x 10^{-5}**

Table A-4. (Continued)

Coal-fired units: organic HAPs	Number of emission factors (1990)	Median emission factor: lb/trillion Btu (1990)	Computer program: 1990 total tons	Number of emission factors (1994)	Median emission factor: lb/trillion Btu (1994)	Computer program: 1994 total tons	Number of emission factors (2010)	Median emission factor: lb/trillion Btu (2010)	Computer program: 2010 total tons
1,2,3,4,7,8,9-heptachlorodi-benzofuran	**4**	**1.8×10^{-5}**	**1.6×10^{-4}**	**5**	**8.3 x 10-6**	**7.4×10^{-5}**	**4**	**1.8×10^{-5}**	**2.1×10^{-4}**
Heptachlorodi-benzofuran	**9**	**1.9×10^{-5}**	**1.6×10^{-4}**	**9**	**1.9×10^{-5}**	**1.7×10^{-4}**	**9**	**1.9×10^{-5}**	**2.2×10^{-4}**
Hexachlorodi-benzofuran	**8**	**2.1×10^{-5}**	**1.8×10^{-4}**	**8**	**2.1×10^{-5}**	**1.9×10^{-4}**	**8**	**2.1×10^{-5}**	**2.4×10^{-4}**
Octachlorodi-benzofuran	**9**	**1.7×10^{-5}**	**1.4×10^{-4}**	**10**	**1.9×10^{-5}**	**1.7×10^{-4}**	**9**	**1.7×10^{-5}**	**1.9×10^{-4}**
Pentachlorodi-benzofuran	**10**	**1.2×10^{-5}**	**1.0×10^{-4}**	**10**	**1.2×10^{-5}**	**1.1×10^{-4}**	**10**	**1.2×10^{-5}**	**1.3×10^{-4}**
Tetrachlorodi-benzofuran	**10**	**1.1×10^{-5}**	**9.8×10^{-5}**	**10**	**1.1×10^{-5}**	**1.0×10^{-4}**	**10**	**1.1×10^{-5}**	**1.3×10^{-4}**
1-methylnaphthalene	**3**	**0.011**	**0.098**	**5**	**0.011**	**0.102**	**3**	**0.01**	**0.132**
2-chloronaphthalene	**3**	**0.040**	**0.352**	**2**	**4.6×10^{-4}**	**0.004**	**3**	**0.04**	**0.462**
2-methylnaphthalene	**6**	**0.032**	**0.275**	**9**	**0.03**	**0.275**	**6**	**0.032**	**0.363**
Acenaphthene	**8**	**0.013**	**0.108**	**9**	**0.017**	**0.154**	**8**	**0.013**	**0.143**
Acenaphthylene	**7**	**0.004**	**0.036**	**10**	**0.0057**	**0.052**	**7**	**0.004**	**0.047**
Anthracene	**7**	**0.004**	**0.039**	**10**	**0.005**	**0.047**	**7**	**0.004**	**0.052**
Benz(a)anthracene	**6**	**0.002**	**0.018**	**9**	**0.004**	**0.040**	**6**	**0.002**	**0.024**
Benzo(a)pyrene	**8**	**0.001**	**0.009**	**7**	**0.0015**	**0.013**	**8**	**0.001**	**0.012**
Benzo(e)pyrene	**4**	**0.001**	**0.012**	**6**	**0.002**	**0.022**	**4**	**0.001**	**0.016**
Benzo(b)fluoranthene	**1**	**0.008**	**0.069**	**2**	**0.005**	**0.048**	**1**	**0.008**	**0.092**
Benzo(b+k)fluoranthene	**3**	**0.004**	**0.036**	**4**	**0.004**	**0.039**	**3**	**0.004**	**0.048**
Benzo(k)fluoranthene	**1**	**0.004**	**0.031**	**3**	**0.001**	**0.011**	**1**	**0.004**	**0.040**
Benzo(g,h,i)perylene	**4**	**0.002**	**0.019**	**6**	**0.002**	**0.017**	**4**	**0.002**	**0.025**
Biphenyl	**4**	**0.18**	**1.562**	**6**	**0.073**	**0.649**	**4**	**0.18**	**2.068**

Table A-4. (Continued)

Coal-fired units: organic HAPs	Number of emission factors (1990)	Median emission factor: lb/trillion Btu (1990)	Computer program: 1990 total tons	Number of emission factors (1994)	Median emission factor: lb/trillion Btu (1994)	Computer program: 1994 total tons	Number of emission factors (2010)	Median emission factor: lb/trillion Btu (2010)	Computer program: 2010 total tons
Chrysene	**6**	**0.003**	**0.022**	**9**	**0.006**	**0.054**	**6**	**0.003**	**0.030**
Dibenzo(a,h)anthracene	**2**	**0.001**	**0.011**	**5**	**7.0×10^{-4}**	**0.006**	**2**	**0.001**	**0.015**
Fluoranthene	**8**	**0.016**	**0.132**	**10**	**0.025**	**0.220**	**8**	**0.016**	**0.176**
Fluorene	**7**	**0.013**	**0.110**	**10**	**0.015**	**0.132**	**7**	**0.013**	**0.154**
Indeno(1,2,3-c,d)pyrene	**4**	**0.003**	**0.028**	**8**	**0.002**	**0.021**	**4**	**0.003**	**0.037**
Phenanthrene	**7**	**0.032**	**0.275**	**10**	**0.072**	**0649**	**7**	**0.032**	**0.363**
Pyrene	**7**	**0.012**	**0.106**	**10**	**0.013**	**0.121**	**7**	**0.012**	**0.143**

1.1 Bituminous And Subbituminous Coal Combustion

1.1.1 General

Coal is a complex combination of organic matter and inorganic mineral matter formed over eons from successive layers of fallen vegetation. Coals are classified by rank according to their progressive alteration in the natural metamorphosis from lignite to anthracite. Coal rank depends on the volatile matter, fixed carbon, inherent moisture, and oxygen, although no single parameter defines a rank. Typically, coal rank increases as the amount of fixed carbon increases and the amount of volatile matter and moisture decreases.

Bituminous coals are by far the largest group and are characterized as having lower fixed carbon and higher volatile matter than anthracite. The key distinguishing characteristics of bituminous coal are its relative volatile matter and sulfur content as well as its slagging and agglomerating characteristics. Subbituminous coals have higher moisture and volatile matter and lower sulfur content than bituminous coals and may be used as an alternative fuel in some boilers originally designed to burn bituminous coals.[1] Generally, bituminous coals have heating values of 10,500 to 14,000 British thermal units per pound (Btu/lb) on a wet, mineral-matter-free basis.[2] As mined, the heating values of typical U.S. bituminous coals range from 10,720 to 14,730 Btu/lb.[3] The heating values of subbituminous coals range from 8,300 to 11,500 Btu/lb on a wet, mineral-matter-free basis[2], and from 9,420 to 10,130 Btu/lb on an as-mined basis.[3] Formulae and tables for classifying coals are given in Reference 2.

1.1.2 Firing Practices[4]

Coal-fired boilers can be classified by type, fuel, and method of construction. Boiler types are identified by the heat transfer method (watertube, firetube, or cast iron), the arrangement of the heat transfer surfaces (horizontal or vertical, straight or bent tube), and the firing configuration (suspension, stoker, or fluidized bed). The most common heat transfer method for coal-fired boilers is the watertube method in which the hot combustion gases contact the outside of the heat transfer tubes, while the boiler water and steam are contained within the tubes.

Coal-fired watertube boilers include pulverized coal, cyclone, stoker, fluidized bed, and handfed units. In stoker-fired systems and most handfed units, the fuel is primarily burned on the bottom of the furnace or on a grate. In a fluidized bed combustor (FBC), the coal is introduced to a bed of either sorbent or inert material (usually sand) which is fluidized by an upward flow of air. In pulverized coal-fired (PC-fired) boilers, the fuel is pulverized to the consistency of talcum powder (i.e., at least 70 percent of the particles will pass through a 200-mesh sieve) and pneumatically injected through the burners into the furnace. Combustion in PC-fired units takes place almost entirely while the coal is suspended in the furnace volume. PC-fired boilers are classified as either dry bottom or wet bottom (also referred to as slag tap furnaces), depending on whether the ash is removed in a solid or molten state. In dry bottom furnaces, coals with high fusion temperatures are burned, resulting in dry ash. In wet bottom furnaces, coals with low fusion temperatures are used, resulting in molten ash or slag.

Depending upon the type and location of the burners and the direction of coal injection into the furnace, PC-fired boilers can also be classified into two different firing types, including wall, and tangential. Wall-fired boilers can be either single wall-fired, with burners on only one wall of the furnace firing horizontally, or opposed wall-fired, with burners mounted on two opposing walls. Tangential (or corner-fired) boilers have burners mounted in the corners of the furnace. The fuel and air are injected tangent to an imaginary circle in the plane of the boilers. Cyclone furnaces are often categorized as PC-fired systems even though the coal is crushed to a maximum size of about 4-mesh. The coal is fed tangentially, with primary air, into a horizonal cylindrical furnace. Smaller coal particles are burned in suspension while larger particles adhere to the molten layer of slag on the combustion chamber wall. Cyclone boilers are high-temperature, wet-bottom type systems.

Stoker-fired systems account for the vast majority of coal-fired watertube boilers for industrial, commercial, and institutional applications. Most packaged stoker units designed for coal firing are small and can be divided into three groups: underfeed stokers, overfeed stokers, and spreader stokers. Underfeed stokers are generally either the horizontal-feed, side-ash-discharge type or the gravity-feed, rear-ash-discharge type. An overfeed stoker uses a moving grate assembly in which coal is fed from a hopper onto a continuous grate which conveys the fuel into the furnace. In a spreader stoker, mechanical or pneumatic feeders distribute coal uniformly over the surface of a moving grate. The injection of the fuel into the furnace and onto the grate combines suspension burning with a thin, fast-burning fuel bed. The amount of fuel burned in suspension depends primarily on fuel size and composition, and air flow velocity. Generally, fuels with finer size distributions, higher volatile matter contents, and lower moisture contents result in a greater percentage of combustion and corresponding heat release rates in suspension above the bed.

FBCs, while not constituting a significant percentage of the total boiler population, have nonetheless gained popularity in the last decade, and today generate steam for industries, cogenerators, independent power producers, and utilities. There are two major categories of FBC systems: (1) atmospheric, operating at or near ambient pressures, and (2) pressurized, operating from 4 to 30 atmospheres (60 to 450 pounds per square inch gauge). At this time, atmospheric FBCs are more advanced (or commercialized) than pressurized FBCs. The two principal types of atmospheric FBCs are bubbling bed and circulating bed. The feature that varies most fundamentally between these two types is the fluidization velocity. In the bubbling bed design, the fluidation velocity is relatively low in order to minimize solids carryover or elutriation from the combustor. Circulating FBCs, however, employ high fluidization velocities to promote the carryover or circulation of the solids. High-temperature cyclones are used in circulating FBCs and in some bubbling FBCs to capture the solid fuel and bed material for return to the primary combustion chamber. The circulating FBC maintains a continuous, high-volume recycle rate which increases the residence time compared to the bubbling bed design. Because of this feature, circulating FBCs often achieve higher combustion efficiencies and better sorbent utilization than bubbling bed units.

Small, coal-fired boilers and furnaces are found in industrial, commercial, institutional, or residential applications and are sometimes capable of being hand-fired. The most common types of firetube boilers used with coal are the horizontal return tubular (HRT), Scotch, vertical, and the firebox. Cast iron boilers are also sometimes available as coal-fired units in a handfed configuration. The HRT boilers are generally fired with gas or oil instead of coal. The boiler and furnace are contained in the same shell in a Scotch or shell boiler. Vertical firetube boilers are typically small singlepass units in which the firetubes come straight up from the water-cooled combustion chamber located at the bottom of the unit. A firebox boiler is constructed with an internal steel-encased, water-jacketed firebox. Firebox firetube boilers are also referred to as locomotive, short firebox, and compact firebox boilers and employ mechanical stokers or are hand-fired.

1.1.3 Emissions[4]

Emissions from coal combustion depend on the rank and composition of the fuel, the type and size of the boiler, firing conditions, load, type of control technologies, and the level of equipment maintenance. The major pollutants of concern from bituminous and subbituminous coal combustion are particulate matter (PM), sulfur oxides (SO_x), and nitrogen oxides (NO_x). Some unburned combustibles, including carbon monoxide (CO) and numerous organic compounds, are generally emitted even under proper boiler operating conditions.

1.1.3.1 Particulate Matter[4] -

PM composition and emission levels are a complex function of boiler firing configuration, boiler operation, pollution control equipment, and coal properties. Uncontrolled PM emissions from coal-fired boilers include the ash from combustion of the fuel as well as unburned carbon resulting from incomplete combustion. In pulverized coal systems, combustion is almost complete; thus, the emitted PM is primarily composed of inorganic ash residues.

Coal ash may either settle out in the boiler (bottom ash) or entrained in the flue gas (fly ash). The distribution of ash between the bottom ash and fly ash fractions directly affects the PM emission rate and depends on the boiler firing method and furnace type (wet or dry bottom). Boiler load also affects the PM emissions as decreasing load tends to reduce PM emissions. However, the magnitude of the reduction varies considerably depending on boiler type, fuel, and boiler operation.

Soot blowing is also a source of intermittent PM emissions in coal-fired boilers. Steam soot and air soot blowing is periodically used to dislodge ash from heat transfer surfaces in the furnace, convective section, economizer, and air preheater.

Particulate emissions may be categorized as either filterable or condensable. Filterable emissions are generally considered to be the particles that are trapped by the glass fiber filter in the front half of a Reference Method 5 or Method 17 sampling train. Vapors and particles less than 0.3 microns pass through the filter. Condensable particulate matter is material that is emitted in the vapor state which later condenses to form homogeneous and/or heterogeneous aerosol particles. The condensable particulate emitted from boilers fueled on coal or oil is primarily inorganic in nature.

1.1.3.2 Sulfur Oxides[4] -

Gaseous SO_x from coal combustion are primarily sulfur dioxide (SO_2), with a much lower quantity of sulfur trioxide (SO_3) and gaseous sulfates. These compounds form as the organic and pyritic sulfur in the coal are oxidized during the combustion process. On average, about 95 percent of the sulfur present in bituminous coal will be emitted as gaseous SO_x, whereas somewhat less will be emitted when subbituminous coal is fired. The more alkaline nature of the ash in some subbituminous coals causes some of the sulfur to react in the furnace to form various sulfate salts that are retained in the boiler or in the flyash.

1.1.3.3 Nitrogen Oxides[5-6] -

NO_x emissions from coal combustion are primarily nitric oxide (NO), with only a few volume percent as nitrogen dioxide (NO_2). Nitrous oxide (N_2O) is also emitted at a few parts per million. NO_x formation results from thermal fixation of atmospheric nitrogen in the combustion flame and from oxidation of nitrogen bound in the coal. Experimental measurements of thermal NO_x formation have shown that the NO_x concentration is exponentially dependent on temperature and is proportional to nitrogen concentration in the flame, the square root of oxygen concentration in the flame, and the gas residence time.[7] Cyclone boilers typically have high conversion of nitrogen to NO_x Typically, only 20 to 60 percent of the fuel nitrogen is converted to NO_x. Bituminous and subbituminous coals usually contain from 0.5 to 2 weight percent nitrogen, mainly present in aromatic ring structures. Fuel nitrogen can account for up to 80 percent of total NO_x from coal combustion.

1.1.3.4 Carbon Monoxide -

The rate of CO emissions from combustion sources depends on the fuel oxidation efficiency of the source. By controlling the combustion process carefully, CO emissions can be minimized. Thus, if a unit is operated improperly or is not well-maintained, the resulting concentrations of CO (as well as organic compounds) may increase by several orders of magnitude. Smaller boilers, heaters, and furnaces typically emit more CO and organics than larger combustors. This is because smaller units usually have less high-temperature residence time and, therefore, less time to achieve complete combustion than larger combustors. Combustion modification techniques and equipment used to reduce NO_x can increase CO emissions if the modification techniques are improperly implemented or if the equipment is improperly designed.

1.1.3.5 Organic Compounds -

As with CO emissions, the rate at which organic compounds are emitted depends on the combustion efficiency of the boiler. Therefore, combustion modifications that change combustion residence time, temperature, or turbulence may increase or decrease concentrations of organic compounds in the flue gas.

Organic emissions include volatile, semivolatile, and condensable organic compounds either present in the coal or formed as a product of incomplete combustion (PIC). Organic emissions are primarily characterized by the criteria pollutant class of unburned vapor-phase hydrocarbons. These emissions include alkanes, alkenes, aldehydes, alcohols, and substituted benzenes (e.g., benzene, toluene, xylene, and ethyl benzene). [8,9]

Emissions of polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans (PCDD/PCDF) also result from the combustion of coal. Of primary interest environmentally are tetrachloro- through octachloro- dioxins and furans. Dioxin and furan emissions are influenced by the extent of destruction of organics during combustion and through reactions in the air pollution control equipment. The formation of PCDD/PCDF in air pollution control equipment is primarily dependent on flue gas temperature, with maximum potential for formation occurring at flue gas temperatures of 450 degrees to 650 degrees Fahrenheit.

The remaining organic emissions are composed largely of compounds emitted from combustion sources in a condensed phase. These compounds can almost exclusively be classed into a group known as polycyclic organic matter (POM), and a subset of compounds called polynuclear aromatic hydrocarbons (PNA or PAH). Polycyclic organic matter is more prevalent in the emissions from coal combustion because of the more complex structure of coal.

1.1.3.6 Trace Metals-

Trace metals are also emitted during coal combustion. The quantity of any given metal emitted, in general, depends on:

- the physical and chemical properties of the metal itself;

- the concentration of the metal in the coal;

- the combustion conditions; and

- the type of particulate control device used, and its collection efficiency as a function of particle size.

Some trace metals become concentrated in certain particle streams from a combustor (e.g., bottom ash, collector ash, and flue gas particulate) while others do not.[10] Various classification schemes have been developed to describe this partitioning behavior.[10-12] These classification schemes generally distinguish between:

- Class 1: Elements that are approximately equally concentrated in the fly ash and bottom ash, or show little or no small particle enrichment. Examples include manganese, beryllium, cobalt, and chromium.

- Class 2: Elements that are enriched in fly ash relative to bottom ash, or show increasing enrichment with decreasing particle size. Examples include arsenic, cadmium, lead, and antimony.

- Class 3: Elements which are emitted in the gas phase (primarily mercury and, in some cases, selenium).

Control of Class 1 metals is directly related to control of total particulate matter emissions, while control of Class 2 metals depends on collection of fine particulate. Because of variability in particulate control device efficiencies, emission rates of these metals can vary substantially. Because of the volatility of Class 3 metals, particulate controls have only a limited impact on emissions of these metals.

1.1.3.7 Acid Gases-

In addition to SO_2 and NO_x emissions, combustion of coal also results in emissions of chlorine and fluorine, primarily in the form of hydrogen chloride (HCl) and hydrogen fluoride (HF). Lesser amounts of chlorine gas and fluorine gas are also emitted. A portion of the chlorine and fluorine in the fuel may be absorbed onto fly ash or bottom ash. Both HCl and HF are water soluble and are readily controlled by acid gas scrubbing systems.

1.1.3.8 Fugitive Emissions -

Fugitive emissions are defined as pollutants which escape from an industrial process due to leakage, materials handling, inadequate operational control, transfer, or storage. The fly ash handling operations in most modern utility and industrial combustion sources consist of pneumatic systems or enclosed and hooded systems which are vented through small fabric filters or other dust control devices. The fugitive PM emissions from these systems are therefore minimal. Fugitive particulate emissions can sometimes occur during fly ash transfer operations from silos to trucks or rail cars.

1.1.3.9 Greenhouse Gases[13-18] -

Carbon dioxide (CO_2), methane (CH_4), and nitrous oxide (N_2O) emissions are all produced during coal combustion. Nearly all of the fuel carbon (99 percent) in coal is converted to CO_2 during the combustion process. This conversion is relatively independent of firing configuration. Although the formation of CO acts to reduce CO_2 emissions, the amount of CO produced is insignificant compared to the amount of CO_2 produced. The majority of the fuel carbon not converted to CO_2 is entrained in bottom ash. CO_2 emissions for coal vary with carbon content, and carbon content varies between the classes of bituminous and subbituminous coals. Further, carbon content also varies within each class of coal based on the geographical location of the mine.

Formation of N_2O during the combustion process is governed by a complex series of reactions and its formation is dependent upon many factors. Formation of N_2O is minimized when combustion temperatures are kept high (above 1575°F) and excess air is kept to a minimum (less than 1 percent). N_2O emissions for coal combustion are not significant except for fluidized bed combustion (FBC), where the emissions are typically two orders of magnitude higher than all other types of coal firing due to areas of low temperature combustion in the fuel bed.

Methane emissions vary with the type of coal being fired and firing configuration, but are highest during periods of incomplete combustion, such as the start-up or shut-down cycle for coal-fired boilers. Typically, conditions that favor formation of N_2O also favor emissions of CH_4.

1.1.4 Controls[4]

Control techniques for criteria pollutants from coal combustion may be classified into three broad categories: fuel treatment/substitution, combustion modification, and postcombustion control. Emissions of noncriteria pollutants such as particulate phase metals have been controlled through the use of post combustion controls designed for criteria pollutants. Fuel treatment primarily reduces SO_2 and includes coal cleaning using physical, chemical, or biological processes; fuel substitution involves burning a cleaner fuel. Combustion modification includes any physical or operational change in the furnace or boiler and is applied primarily for NO_x control purposes, although for small units, some reduction in PM emissions may be available through improved combustion practice. Postcombustion control employs a device after the combustion of the fuel and is applied to control emissions of PM, SO_2 , and NO_x for coal combustion.

1.1.4.1 Particulate Matter Control[4] -

The principal control techniques for PM are combustion modifications (applicable to small stoker-fired boilers) and postcombustion methods (applicable to most boiler types and sizes). Uncontrolled PM emissions from small stoker-fired and hand-feed combustion sources can be minimized by employing good combustion practices such as operating within the recommended load ranges, controlling the rate of load changes, and ensuring steady, uniform fuel feed. Proper design and operation of the combustion air delivery systems can also minimize PM emissions. The postcombustion control of PM emissions from coal-fired combustion sources can be accomplished by using one or more or the following particulate control devices:

- Electrostatic precipitator (ESP),
- Fabric filter (or baghouse),
- Wet scrubber,
- Cyclone or multiclone collector, or
- Side stream separator.

Electrostatic precipitation technology is applicable to a variety of coal combustion sources. Because of their modular design, ESPs can be applied to a wide range of system sizes and should have no adverse effect on combustion system performance. The operating parameters that influence ESP performance include fly ash mass loading, particle size distribution, fly ash electrical resistivity, and precipitator voltage and current. Other factors that determine ESP collection efficiency are collection plate area, gas flow velocity, and cleaning cycle. Data for ESPs applied to coal-fired sources show fractional collection efficiencies greater than 99 percent for fine (less than 0.1 micrometer) and coarse particles (greater than 10 micrometers). These data show a reduction in collection efficiency for particle diameters between 0.1 and 10 micrometers.

Fabric filtration has been widely applied to coal combustion sources since the early 1970s and consists of a number of filtering elements (bags) along with a bag cleaning system contained in a main shell structure incorporating dust hoppers. The particulate removal efficiency of fabric filters is dependent on a variety of particle and operational characteristics. Particle characteristics that affect the collection efficiency include particle size distribution, particle cohesion characteristics, and particle electrical resistivity. Operational parameters that affect fabric filter collection efficiency include air-to-cloth ratio, operating pressure loss, cleaning sequence, interval between cleanings, cleaning method, and cleaning intensity. In addition, the particle collection efficiency and size distribution can be affected by certain fabric properties (e. g., structure of fabric, fiber composition, and bag properties). Collection efficiencies of fabric filters can be as high as 99.9 percent.

Wet scrubbers, including venturi and flooded disc scrubbers, tray or tower units, turbulent contact absorbers, or high-pressure spray impingement scrubbers are applicable for PM as well as SO_2 control on coal-fired combustion sources. Scrubber collection efficiency depends on particle size distribution, gas side pressure drop through the scrubber, and water (or scrubbing liquor) pressure, and can range between 95 and 99 percent for a 2-micron particle.

Cyclone separators can be installed singly, in series, or grouped as in a multicyclone or multiclone collector. These devices are referred to as mechanical collectors and are often used as a precollector upstream of an ESP, fabric filter, or wet scrubber so that these devices can be specified for lower particle loadings to reduce capital and/or operating costs. The collection efficiency of a mechanical collector depends strongly on the effective aerodynamic particle diameter. Although these devices will reduce PM emissions from coal combustion, they are relatively ineffective for collection of particles less than 10 micron (PM-10). The typical overall collection efficiency for mechanical collectors ranges from 90 to 95 percent.

The side-stream separator combines a multicyclone and a small pulse-jet baghouse to more efficiently collect small-diameter particles that are difficult to capture by a mechanical collector alone. Most applications to date for side-stream separators have been on small stoker boilers.

Atmospheric fluidized bed combustion (AFBC) boilers may tax conventional particulate control systems. The particulate mass concentration exiting AFBC boilers is typically 2 to 4 times higher than pulverized coal boilers. AFBC particles are also, on average, smaller in size, and irregularly shaped with higher surface area and porosity relative to pulverized coal ashes. The effect is a higher pressure drop. The AFBC ash is more difficult to collect in ESPs than pulverized coal ash because AFBC ash has a higher electrical resistivity and the use of multiclones for recycling, inherent with the AFBC process, tends to reduce exit gas stream particulate size.

1.1.4.2 Sulfur Oxides Control[4] -

Several techniques are used to reduce SO_x emissions from coal combustion. Table 1.1-1 presents the techniques most frequently used. One way is to switch to lower sulfur coals, since SO_x emissions are proportional to the sulfur content of the coal. This alternative may not be possible where lower sulfur coal is not readily available or where a different grade of coal cannot be satisfactorily fired. In some cases, various coal cleaning processes may be employed to reduce the fuel sulfur content. Physical coal cleaning removes mineral sulfur such as pyrite but is not effective in removing organic sulfur. Chemical cleaning and solvent refining processes are being developed to remove organic sulfur.

Post combustion flue gas desulfurization (FGD) techniques can remove SO_2 formed during combustion by using an alkaline reagent to absorb SO_2 in the flue gas. Flue gases can be treated using wet, dry, or semi-dry desulfurization processes of either the throwaway type (in which all waste streams are discarded) or the recovery/regenerable type (in which the SO_2 absorbent is regenerated and reused). To date, wet systems are the most commonly applied. Wet systems generally use alkali slurries as the SO_2 absorbent medium and can be designed to remove greater than 90 percent of the incoming SO_2. Lime/limestone scrubbers, sodium scrubbers, and dual alkali scrubbers are among the commercially proven wet FGD systems. The effectiveness of these devices depends not only on control device design but also on operating variables. Particulate reduction of more than 99 percent is possible with wet scrubbers, but fly ash is often collected by upstream ESPs or baghouses, to avoid erosion of the desulfurization equipment and possible interference with FGD process reactions.[18] Also, the volume of scrubber sludge is reduced with separate fly ash removal, and contamination of the reagents and by-products is prevented.

The lime and limestone wet scrubbing process uses a slurry of calcium oxide or limestone to absorb SO_2 in a wet scrubber. Control efficiencies in excess of 91 percent for lime and 94 percent for limestone over extended periods are possible. Sodium scrubbing processes generally employ a wet scrubbing solution of sodium hydroxide or sodium carbonate to absorb SO_2 from the flue gas. Sodium scrubbers are generally limited to smaller sources because of high reagent costs and can have SO_2 removal efficiencies of up to 96.2 percent. The double or dual alkali system uses a clear sodium alkali solution for SO_2 removal followed by a regeneration step using lime or limestone to recover the sodium alkali and produce a calcium sulfite and sulfate sludge. SO_2 removal efficiencies of 90 to 96 percent are possible.

1.1.4.3 Nitrogen Oxide Controls[4] -

Several techniques are used to reduce NO_x emissions from coal combustion. These techniques are summarized in Table 1.1-2. The primary techniques can be classified into one of two fundamentally different methods—combustion controls and postcombustion controls. Combustion controls reduce NO_x by suppressing NO_x formation during the combustion process, while postcombustion controls reduce NO_x emission after their formation. Combustion controls are the most widely used method of controlling NO_x formation in all types of boilers and include low excess air (LEA), burners out of service (BOOS), biased burner firing, overfire air (OFA), low NO_x burners (LNBs), and reburn. Postcombustion control methods are selective noncatalytic reduction (SNCR) and selective catalytic reduction (SCR). Combustion and postcombustion controls can be used separately or combined to achieve greater NO_x reduction from fluidized bed combustors in boilers.

Operating at LEA involves reducing the amount of combustion air to the lowest possible level while maintaining efficient and environmentally compliant boiler operation. NO_x formation is inhibited because less oxygen is available in the combustion zone. BOOS involves withholding fuel flow to all or part of the top row of burners so that only air is allowed to pass through. This method simulates air staging, or OFA conditions, and limits NO_x formation by lowering the oxygen level in the burner area. Biased burner firing involves more fuel-rich firing in the lower rows of burners than in the upper row of burners. This method provides a form of air staging and limits NO_x formation by limiting the amount of oxygen in the firing zone. These methods may change the normal operation of the boiler and the effectiveness is boiler-specific. Implementation of these techniques may also reduce operational flexibility; however, they may reduce NO_x by 10 to 20 percent from uncontrolled levels.

OFA is a technique in which a percentage of the total combustion air is diverted from the burners and injected through ports above the top burner level. OFA limits NO_x by (1) suppressing thermal NO_x by partially delaying and extending the combustion process resulting in less intense combustion and cooler flame temperatures and (2) suppressing fuel NO_x formation by reducing the concentration of air in the combustion zone where volatile fuel nitrogen is evolved. OFA can be applied for various boiler types including tangential and wall-fired, turbo, and stoker boilers and can reduce NO_x by 20 to 30 percent from uncontrolled levels.

LNBs limit NO_x formation by controlling the stoichiometric and temperature profiles of the combustion process in each burner zone. The unique design of features of an LNB may create (1) a reduced oxygen level in the combustion zone to limit fuel NO_x formation, (2) a reduced flame temperature that limits thermal NO_x formation, and/or (3) a reduced residence time at peak temperature which also limits thermal NO_x formation.

LNBs are applicable to tangential and wall-fired boilers of various sizes but are not applicable to other boiler types such as cyclone furnaces or stokers. They have been used as a retrofit NO_x control for existing boilers and can achieve approximately 35 to 55 percent reduction from uncontrolled levels. They are also used in new boilers to meet New Source Performance Standards (NSPS) limits. LNBs can be combined with OFA to achieve even greater NO_x reduction (40 to 60 percent reduction from uncontrolled levels).

Reburn is a combustion hardware modification in which the NO_x produced in the main combustion zone is reduced in a second combustion zone downstream. This technique involves withholding up to 40 percent (at full load) of the heat input to the main combustion zone and introducing that heat input above the top row of burners to create a reburn zone. Reburn fuel (natural gas, oil, or pulverized coal) is injected with either air or flue gas to create a fuel-rich zone that reduces the NO_x created in the main combustion zone to nitrogen and water vapor. The fuel-rich combustion gases from the reburn zone are completely combusted by injecting overfire air above the reburn zone. Reburn may be applicable to many boiler types firing coal as the primary fuel, including tangential, wall-fired, and cyclone boilers. However, the application and effectiveness are site-specific because each boiler is originally designed to achieve specific steam conditions and capacity which may be altered due to reburn. Commercial experience is limited; however, this limited experience does indicate NO_x reduction of 50 to 60 percent from uncontrolled levels may be achieved.

SNCR is a postcombustion technique that involves injecting ammonia (NH_3) or urea into specific temperature zones in the upper furnace or convective pass. The ammonia or urea reacts with NO_x in the flue gas to produce nitrogen and water. The effectiveness of SNCR depends on the temperature where reagents are injected; mixing of the reagent in the flue gas; residence time of the reagent within the required temperature window; ratio of reagent to NO_x; and the sulfur content of the fuel that may create sulfur compounds that deposit in downstream equipment. There is not as much commercial experience to base effectiveness on a wide range of boiler types; however, in limited applications, NO_x reductions of 25 to 40 percent have been achieved.

SCR is another postcombustion technique that involves injecting NH_3 into the flue gas in the presence of a catalyst to reduce NO_x to nitrogen and then water. The SCR reactor can be located at various positions in the process including before an air heater and particulate control device, or downstream of the air heater, particulate control device, and flue gas desulfurization systems. The performance of SCR is influenced by flue gas temperature, fuel sulfur content, ammonia-to-NO_x ratio, inlet NO_x concentration, space velocity, and catalyst condition. Although there is currently very limited application of SCR in the U.S. on coal-fired boilers, NO_x reductions of 75 to 86 percent have been realized on a few pilot systems.

1.1.5 Emission Factors

Emission factors for SO_x, NO_x, and CO are presented in Table 1.1-3. Tables in this section present emission factors on both a weight basis (lb/ton) and an energy basis (lb/Btu). To convert from lb/ton to lb/MMBtu, divide by a heating value of 26.0 MMBtu/ton. Because of the inherently low NO_X emission characteristics of FBCs and the potential for in-bed SO_2 capture by calcium-based sorbents, uncontrolled emission factors for this source category were not developed in the same sense as with other source categories. For NO_x emissions, the data collected from test reports were considered to be baseline (uncontrolled) if no additional add-on NO_x control system (such as ammonia injection) was operated.

For SO_2 emissions, a correlation was developed from reported data on FBCs to relate SO_2 emissions to the coal sulfur content and the calcium-to-sulfur ratio in the bed.

Filterable particulate matter and particulate matter less than, or equal to, 10 micrometers in diameter (PM-10) emission factors are presented in Table 1.1-4. Condensable particulate matter emission factors are presented in Table 1.1.5. Cumulative particle size distributions and particulate size-specific emission factors are given in Tables 1.1-6, 1.1-7, 1.1-8, 1.1-9, 1.1-10, and 1.1-11. Particulate size-specific emission factors are also presented graphically in Figures 1.1-1, 1.1-2, 1.1-3, 1.1-4, 1.1-5, and 1.1-6.

Controlled emission factors for PCDD/PCDF and PAHs are provided in Tables 1.1-12 and 1.1-13, respectively. Controlled emission factors for other organic compounds are presented in Table 1.1-14. Emission factors for hydrogen chloride and hydrogen fluoride are presented in Table 1.1-15.

Table 1.1-16 presents emission factor equations for nine trace metals from controlled and uncontrolled boilers. Table 1.1-17 presents uncontrolled emission factors for seven of the same metals, along with mercury, POM and formaldehyde. Table 1.1-18 presents controlled emission factors for 13 trace metals and includes the metals found in Tables 1.1-16 and 1.1-17. The emission factor equations in Table 1.1-16 are based on statistical correlations among measured trace element concentrations in coal, measured fractions of ash in coal, and measured particulate matter emission factors. Because these are the major parameters affecting trace metals emissions from coal combustion, it is recommended that the emission factor equations be used when the inputs to the equations are available. If the inputs to the emission factor equations are not available for a pollutant, then the emission factors provided in Table 1.1-17 and 1.1-18 for the pollutant should be used.

Greenhouse gas emission factors, including CH_4, non-methane organic compounds (NMOC), and N_2O are provided in Table 1.1-19. In addition, Table 1.1-20 provides emission factors for CO_2.

1.1.6 Updates Since the Fifth Edition

The Fifth Edition was released in January 1995. Revisions to this section since that date are summarized below. For further detail, consult the memoranda describing each supplement or the background report for this section. These and other documents can be found on the CHIEF home page (http://www.epa.gov/ttn/chief/).

Supplement A, February 1996

- SCC's were corrected from 1-01-002-17, 1-02-002-17, and 1-03-002-17, to 1-01-002-18, 1-02-002-18, and 1-03-002-18 in the tables with SO_x, NO_x, CO, and PM/PM10 emission factors.

- For SO_x factors, clarifications were added to the table footnotes to clarify that "S" is a weight percent and not a fraction. Similar clarification was added to the footnote for the CO_2 factor.

- For fluidized bed combustors (bubbling bed and circulating bed), the PM10 factors were replaced with footnote "m." The revised footnote "m" directs the user to the emission factor for spreader stoker with multiple cyclones and no flyash reinjection.

- In the table with filterable PM factors, the misspelling of "filterable" was corrected.

- In the cumulative particle size distribution table, text was added to the table footnotes to clarify that "A" is a weight percent and not a fraction.

- In the cumulative particle size distribution for spreader stokers, all of the factors were corrected.

- The N_2O emission factor for bubbling bed was changed from 5.9 lb/ton to 5.5 lb/ton.

Supplement B, October 1996

- Text was added concerning coal rank/classification, firing practices, emissions, and controls.

- The table for NO_x control technologies was revised to include controls for all types of coal-fired boilers.

- SO_x, NO_x, and CO emission factors were added for cell burners.

- The PM table was revised to recommend using spreader stoker PM factors for FBC units.

- Tables were added for new emission factors for polychlorinated toxics, polynuclear aromatics, organic toxics, acid gas toxics, trace metal toxics, and controlled toxics.

- N_2O emission factors were added.

- Default CO_2 emission factors were added.

Supplement E, September 1998

- The term "Filterable" was added to the PM-10 column heading of Table 1.1-4.

- Reference to condensable particulate matter was deleted from footnote b of Table 1.1-4.

- Emission factors for condensable particulate matter were added (Table 1.1-5).

- Table 1.1-7 was revised to correct a typographical errors in the ESP column.

- The zeros in Table 1.1-8 appeared to be in error. Engineering judgement was used to determine a conservative estimate.

- NO_x emission factors were updated based on data from the Acid Rain program.

Table 1.1-1. POSTCOMBUSTION SO_2 CONTROLS FOR COAL COMBUSTION SOURCES

Control Technology	Process	Typical Control Efficiencies	Remarks
Wet scrubber	Lime/limestone	80 - 95+%	Applicable to high sulfur fuels, wet sludge product
	Sodium carbonate	80 - 98%	5-430 million Btu/hr typical application range, high reagent costs
	Magnesium oxide/ hydroxide	80 - 95+%	Can be regenerated
	Dual alkali	90 - 96%	Uses lime to regenerate sodium-based scrubbing liquor
Spray drying	Calcium hydroxide slurry, vaporizes in spray vessel	70 - 90%	Applicable to low and medium sulfur fuels, produces dry product
Furnace injection	Dry calcium carbonate/hydrate injection in upper furnace cavity	25 - 50%	Commercialized in Europe, several U. S. demonstration projects are completed
Duct injection	Dry sorbent injection into duct, sometimes combined with water spray	25 - 50+%	Several research and development, and demonstration projects underway, not yet commercially available in the United States.

Table 1.1-2. NO_x CONTROL OPTIONS FOR COAL-FIRED BOILERS[a]

Control Technique	Description of Technique	Applicable Boiler Designs	NO_x Reduction Potential[b] (%)	Commercial Availability/R & D Status	Comments
Combustion Modifications					
Load reduction	Reduction of coal and air	Stokers	Minimal	Available	Applicable to stokers that can reduce load without increasing excess air; may cause reduction in boiler efficiency; NO_x reduction varies with percent load reduction.
Operational modifications (BOOS, LEA, BF, or combination)	Rearrangement of air or fuel in the main combustion zone	Pulverized coal boilers (some designs); Stokers (LEA only)	10 - 20	Available	Must have sufficient operational flexibility to achieve NO_x reduction potential without sacrificing boiler performance.
Overfire Air	Injection of air above main combustion zone	Pulverized coal boilers and stokers	20 - 30	Available	Must have sufficient furnace height above top row of burners in order to retrofit this technology to existing boilers.
Low NO_x Burners	New burner designs controlling air-fuel mixing	Pulverized coal boilers	35 - 55	Available	Available in new boiler designs and can be retrofit in existing boilers.
LNB with OFA	Combination of new burner designs and injection of air above main combustion zone	Pulverized coal boilers	40 - 60	Available	Available in new boiler designs and can be retrofit in existing boilers with sufficient furnace height above top row of burners.
Reburn	Injection of reburn fuel and completion air above main combustion zone	Pulverized coal boilers, cyclone furnaces	50 - 60	Commercially available but not widely demonstrated	Reburn fuel can be natural gas, fuel oil, or pulverized coal. Must have sufficient furnace height to retrofit this technology to existing boilers.

Table 1.1-2 (cont.).

Control Technique	Description of Technique	Applicable Boiler Designs	NO_x Reduction Potential[b] (%)	Commercial Availability/R & D Status	Comments
Post-Combustion Modifications					
SNCR	Injection of NH_3 or urea in the convective pass	Pulverized coal boilers, cyclone furnaces, stokers, and fluidized bed boilers	30 - 60	Commercially available but not widely demonstrated	Applicable to new boilers or as a retrofit technology; must have sufficient residence time at correct temperature (1,750°±90°F); elaborate reagent injection system; possible load restrictions on boiler; and possible air preheater fouling by ammonium bisulfate.
SCR	Injection of NH_3 in combination with catalyst material	Pulverized coal boilers, cyclone furnaces	75 - 85	Commercially offered, but not yet demonstrated	Applicable to new boilers or as a retrofit technology provided there is sufficient space; hot-side SCR best on low-sulfur fuel and low fly ash applications; cold-side SCR can be used on high-sulfur/high-ash applications if equipped with an upstream FGD system.
LNB with SNCR	Combination of new burner designs and injection of NH_3 or urea	Pulverized coal boilers	50-80	Commercially offered, but not widely demonstrated as a combined technology	Same as LNB and SNCR alone.
LNB with OFA and SCR	Combination of new burner design, injection of air above combustion zone, and injection of NH_3 or urea	Pulverized coal boiler	85-95	Commercially offered, but not widely demonstrated as a combined technology	Same as LNB, OFA, and SCR alone.

[a] References 20-21.

[b] NO_x reduction potential from uncontrolled levels.

Table 1.1-3. EMISSION FACTORS FOR SO_x, NO_x, AND CO FROM BITUMINOUS AND SUBBITUMINOUS COAL COMBUSTION[a]

Firing Configuration	SCC	SO_x[b]		NO_x[c]		CO[d,e]	
		Emission Factor (lb/ton)	EMISSION FACTOR RATING	Emission Factor (lb/ton)	EMISSION FACTOR RATING	Emission Factor (lb/ton)	EMISSION FACTOR RATING
PC, dry bottom, wall-fired[f], bituminous Pre-NSPS[g]	1-01-002-02 1-02-002-02 1-03-002-06	38S	A	22	A	0.5	A
PC, dry bottom, wall-fired[f], bituminous Pre-NSPS[g] with low-NO_x burner	1-01-002-02 1-02-002-02 1-03-002-06	38S	A	11	A	0.5	A
PC, dry bottom, wall-fired[f], bituminous NSPS[g]	1-01-002-02 1-02-002-02 1-03-002-06	38S	A	12	A	0.5	A
PC, dry bottom, wall-fired[f], sub-bituminous Pre-NSPS[g]	1-01-002-22 1-02-002-22 1-03-002-22	35S	A	12	C	0.5	A
PC, dry bottom, wall fired[f], sub-bituminous NSPS[g]	1-01-002-22 1-02-002-22 1-03-002-22	35S	A	7.4	A	0.5	A
PC, dry bottom, cell burner[h] fired, bituminous	1-01-002-15	38S	A	31	A	0.5	A
PC, dry bottom, cell burner fired, sub-bituminous	1-01-002-35	35S	A	14	E	0.5	A

Table 1.1-3 (cont.).

Firing Configuration	SCC	SO$_x$[b]		NO$_x$[c]		CO[d,e]	
		Emission Factor (lb/ton)	EMISSION FACTOR RATING	Emission Factor (lb/ton)	EMISSION FACTOR RATING	Emission Factor (lb/ton)	EMISSION FACTOR RATING
PC, dry bottom, tangentially fired, bituminous, Pre-NSPS[g]	1-01-002-12 1-02-002-12 1-03-002-16	38S	A	15	A	0.5	A
PC, dry bottom, tangentially fired, bituminous, Pre-NSPS[g] with low-NO$_x$ burner	1-01-002-12 1-02-002-12 1-03-002-16	38S	A	9.7	A	0.5	A
PC, dry bottom, tangentially fired, bituminous, NSPS[g]	1-01-002-12 1-02-002-12 1-03-002-16	38S		10	A	0.5	A
PC, dry bottom, tangentially fired, sub-bituminous, Pre-NSPS[g]	1-01-002-26 1-02-002-26 1-03-002-26	35S	A	8.4	A	0.5	A
PC, dry bottom, tangentially fired, sub-bituminous, NSPS[g]	1-01-002-26 1-02-002-26 1-03-002-26	35S	A	7.2	A	0.5	A
PC, wet bottom, wall-fired[f], bituminous, Pre-NSPS[g]	1-01-002-01 1-02-002-01 1-03-002-05	38S	A	31	D	0.5	A
PC, wet bottom, tangentially fired, bituminous, NSPS[g]	1-01-002-11	38S	A	14	E	0.5	A
PC, wet bottom, wall-fired sub-bituminous	1-01-002-21 1-02B002-21 1-03-002-21	35S	A	24	E	0.5	A

Table 1.1-3 (cont.).

Firing Configuration	SCC	SO_x [b]		NO_x [c]		CO [d,e]	
		Emission Factor (lb/ton)	EMISSION FACTOR RATING	Emission Factor (lb/ton)	EMISSION FACTOR RATING	Emission Factor (lb/ton)	EMISSION FACTOR RATING
Cyclone Furnace, bituminous	1-01-002-03 1-02-002-03 1-03-002-03	38S	A	33	A	0.5	A
Cyclone Furnance, sub-bituminous	1-01-002-23 1-02-002-23 1-03-002-23	35S	A	17	C	0.5	A
Spreader stoker, bituminous	1-01-002-04 1-02-002-04 1-03-002-09	38S	B	11	B	5	A
Spreader Stoker, sub-bituminous	1-01-002-24 1-02-002-24 1-03-002-24	35S	B	8.8	B	5	A
Overfeed stoker[i]	1-01-002-05/25 1-02-002-05/25 1-03-002-07/25	38S (35S)	B	7.5	A	6	B
Underfeed stoker	1-02-002-06 1-03-002-08	31S	B	9.5	A	11	B
Hand-fed units	1-03-002-14	31S	D	9.1	E	275	E

Table 1.1-3 (cont.).

		SO_x[b]		NO_x[c]		CO[d,e]	
Firing Configuration	SCC	Emission Factor (lb/ton)	EMISSION FACTOR RATING	Emission Factor (lb/ton	EMISSION FACTOR RATING	Emission Factor (lb/ton)	EMISSION FACTOR RATING
FBC, circulating bed	1-01-002-18 1-02-002-18 1-03-002-18	**C**[j]	E	5.0	D	18	E
FBC, bubbling bed	1-01-002-17 1-02-002-17 1-03-002-17	**C**[j]	E	15.2	D	18	D

[a] Factors represent uncontrolled emissions unless otherwise specified and should be applied to coal feed, as fired. SCC = Source Classification Code. To convert from lb/ton to kg/Mg, multiply by 0.5.

[b] Expressed as SO_2, including SO_2, SO_3, and gaseous sulfates. Factors in parentheses should be used to estimate gaseous SO_x emissions for subbituminous coal. In all cases, S is weight % sulfur content of coal as fired. Emission factor would be calculated by multiplying the weight percent sulfur in the coal by the numerical value preceding S. For example, if fuel is 1.2% sulfur, then S = 1.2. On average for bituminous coal, 95% of fuel sulfur is emitted as SO_2, and only about 0.7% of fuel sulfur is emitted as SO_3 and gaseous sulfate. An equally small percent of fuel sulfur is emitted as particulate sulfate (References 22-23). Small quantities of sulfur are also retained in bottom ash. With subbituminous coal, about 10% more fuel sulfur is retained in the bottom ash and particulate because of the more alkaline nature of the coal ash. Conversion to gaseous sulfate appears about the same as for bituminous coal.

Table 1.1-3. (cont.)

[c] Expressed as NO_2. Generally, 95 volume % or more of NO_x present in combustion exhaust will be in the form of NO, the rest NO_2 (Reference 6). To express factors as NO, multiply factors by 0.66. All factors represent emissions at baseline operation (i. e., 60 to 110% load and no NO_x control measures).

[d] Nominal values achievable under normal operating conditions. Values 1 or 2 orders of magnitude higher can occur when combustion is not complete.

[e] Emission factors for CO_2 emissions from coal combustion should be calculated using lb CO_2/ton coal = 72.6C, where C is the weight % carbon content of the coal. For example, if carbon content is 85%, then C equals 85.

[f] Wall-fired includes front and rear wall-fired units, as well as opposed wall-fired units.

[g] Pre-NSPS boilers are not subject to any NSPS. NSPS boilers are subject to Subpart D or Subpart Da. Subpart D boilers are boilers constructed after August 17, 1971 and with a heat input rate greater than 250 million Btu per hour (MMBtu/hr). Subpart Da boilers are boilers constructed after September 18, 1978 and with a heat input rate greater than 250 MMBtu/hr.

[h] References 24-27.

[i] Includes traveling grate, vibrating grate, and chain grate stokers.

[j] SO_2 emission factors for fluidized bed combustion are a function of fuel sulfur content and calcium-to-sulfur ratio. For both bubbling bed and circulating bed design, use: lb SO_2/ton coal = $39.6(S)(Ca/S)^{-1.9}$. In this equation, S is the weight percent sulfur in the fuel and Ca/S is the molar calcium-to-sulfur ratio in the bed. This equation may be used when the Ca/S is between 1.5 and 7. When no calcium-based sorbents are used and the bed material is inert with respect to sulfur capture, the emission factor for underfeed stokers should be used to estimate the SO_2 emissions. In this case, the emission factor ratings are E for both bubbling and circulating units.

Table 1.1-4. UNCONTROLLED EMISSION FACTORS FOR PM AND PM-10 FROM BITUMINOUS AND SUBBITUMINOUS COAL COMBUSTION[a]

Firing Configuration	SCC	Filterable PM[b]		Filterable PM-10	
		Emission Factor (lb/ton)	EMISSION FACTOR RATING	Emission Factor (lb/ton)	EMISSION FACTOR RATING
PC-fired, dry bottom, wall-fired	1-01-002-02/22 1-02-002-02/22 1-03-002-06/22	10A	A	2.3A	E
PC-fired, dry bottom, tangentially fired	1-01-002-12/26 1-02-002-12/26 1-03-002-16/26	10A	B	2.3A[c]	E
PC-fired, wet bottom	1-01-002-01/21 1-02-002-01/21 1-03-002-05/21	7A[d]	D	2.6A	E
Cyclone furnace	1-01-002-03/23 1-02-002-03/23 1-03-002-03/23	2A[d]	E	0.26A	E
Spreader stoker	1-01-002-04/24 1-02-002-04/24 1-03-002-09/24	66[e]	B	13.2	E
Spreader stoker, with multiple cyclones, and reinjection	1-01-002-04/24 1-02-002-04/24 1-03-002-09/24	17	B	12.4	E
Spreader stoker, with multiple cyclones, no reinjection	1-01-002-04/24 1-02-002-04/24 1-03-002-09/24	12	A	7.8	E

Table 1.1-4 (cont.).

Firing Configuration	SCC	Filterable PM[b]		Filterable PM-10	
		Emission Factor (lb/ton)	EMISSION FACTOR RATING	Emission Factor (lb/ton)	EMISSION FACTOR RATING
Overfeed stoker[f]	1-01-002-05/25 1-02-002-05/25 1-03-002-07/25	16[g]	C	6.0	E
Overfeed stoker, with multiple cyclones[f]	1-01-002-05/25 1-02-002-05/25 1-03-002-07/25	9[h]	C	5.0	E
Underfeed stoker	1-02-002-06 1-03-002-08	15[j]	D	6.2	E
Underfeed stoker, with multiple cyclone	1-02-002-06 1-03-002-08	11[h]	D	6.2[j]	E
Hand-fed units	1-03-002-14	15	E	6.2[k]	E
FBC, bubbling bed	1-01-002-17 1-02-002-17 1-03-002-17	[m]	E	[m]	E
FBC, circulating bed	1-01-002-18 1-02-002-18 1-03-002-18	[m]	E	[m]	E

[a] Factors represent uncontrolled emissions unless otherwise specified and should be applied to coal feed, as fired. To convert from lb/ton to kg/Mg, multiply by 0.5. SCC = Source Classification Code.

Table 1.1-4 (cont.).

[b] Based on EPA Method 5 (front half catch) as described in Reference 28. Where particulate is expressed in terms of coal ash content, A, factor is determined by multiplying weight % ash content of coal (as fired) by the numerical value preceding the A. For example, if coal with 8% ash is fired in a PC-fired, dry bottom unit, the PM emission factor would be 10 x 8, or 80 lb/ton.

[c] No data found; emission factor for PC-fired dry bottom boilers used.

[d] Uncontrolled particulate emissions, when no fly ash reinjection is employed. When control device is installed, and collected fly ash is reinjected to boiler, particulate from boiler reaching control equipment can increase up to a factor of 2.

[e] Accounts for fly ash settling in an economizer, air heater, or breaching upstream of control device or stack. (Particulate directly at boiler outlet typically will be twice this level.) Factor should be applied even when fly ash is reinjected to boiler from air heater or economizer dust hoppers.

[f] Includes traveling grate, vibrating grate, and chain grate stokers.

[g] Accounts for fly ash settling in breaching or stack base. Particulate loadings directly at boiler outlet typically can be 50% higher.

[h] See Reference 4 for discussion of apparently low multiple cyclone control efficiencies, regarding uncontrolled emissions.

[j] Accounts for fly ash settling in breaching downstream of boiler outlet.

[k] No data found; emission factor for underfeed stoker used.

[m] No data found; use emission factor for spreader stoker with multiple cyclones and reinjection.

Table 1.1-5. CONDENSABLE PARTICULATE MATTER EMISSION FACTORS FOR BITUMINOUS AND SUBBITUMINOUS COAL COMBUSTION[a]

Firing Configuration[b]	Controls[c]	SCC	CPM - TOT[d, e]		CPM - IOR[d, e]		CPM - ORG[d, e]	
			Emission Factor (lb/MMBtu)	EMISSION FACTOR RATING	Emission Factor (lb/MMBtu)	EMISSION FACTOR RATING	Emission Factor (lb/MMBtu)	EMISSION FACTOR RATING
All pulverized coal-fired boilers	All PM controls (without FGD controls)	1-01-002-01/21 1-01-002-02/22 1-01-002-12/26 1-02-002-01/21 1-02-002-02/22 1-02-002-12/26 1-03-002-05/06 1-03-002-16 1-03-002-21/22 1-03-002-26	0.1S-0.03[f,g]	B	80% of CPM-TOT emission factor[e]	E	20% of CPM-TOT emission factor[e]	E
All pulverized coal-fired boilers	All PM controls combined with an FGD control	1-01-002-01/21 1-01-002-02/22 1-01-002-12/26 1-02-002-01/21 1-02-002-02/22 1-02-002-12/26 1-03-002-05/06 1-03-002-16 1-03-002-21/22 1-03-002-26	0.02[h]	E	ND		ND	
Spreader stoker, travelling grate overfeed stoker, underfeed stoker	All PM controls, or Uncontrolled	1-01-002-04/24 1-01-002-05/25 1-02-002-04/24 1-02-002-05/25 1-02-002-06 1-03-002-07/08 1-03-002-09/11 1-03-002-16 1-03-002-24/25	0.04[i]	C	80% of CPM-TOT emission factor[g]	E	20% of CPM-TOT emission factor[g]	E

Table 1.1-5 (cont.).

[a] All condensable PM is assumed to be less than 1.0 micron in diameter.

[b] No data are available for cyclone boilers (SCCs 1-01-002-03/23, 1-02-002-03/23, 1-03-002-23) or for atmospheric fluidized bed combustion (AFBC) boilers (SCCs 1-01B002-17, 1-02-002-17, 1-03-002-17). For cyclone boilers, use the factors provided for pulverized coal-fired boilers and applicable control devices. For AFBC boilers, use the factors provided for pulverized coal-fired boilers with PM and FGD controls.

[c] FGD = flue gas desulfurization.

[d] CPM-TOT = total condensable particulate matter.
CPM-IOR = inorganic condensable particulate matter.
CPM-ORG = organic condensable particulate matter.
ND = No data.

[e] Factors should be multiplied by fuel rate on a heat input basis (MMBtu), as fired. To convert to lb/ton of bituminous coal, multiply by 26 MMBtu/ton. To convert to lb/ton of subbituminous coal, multiply by 20 MMBtu/ton.

[f] S = coal sulfur percent by weight, as fired. For example, if the sulfur percent is 1.04, then S = 1.04. If the coal sulfur percent is 0.4 or less, use a default emission factor of 0.01 lb/MMBtu rather than the emission equation.

[g] References 78-94.

[h] References 95 and 96.

[i] References 97-104.

Table 1.1-6. CUMULATIVE PARTICLE SIZE DISTRIBUTION AND SIZE-SPECIFIC EMISSION FACTORS FOR DRY BOTTOM BOILERS BURNING PULVERIZED BITUMINOUS AND SUBBITUMINOUS COAL[a]

Particle Size[b] (μm)	Cumulative Mass % ≤ Stated Size					Cumulative Emission Factor[c] (lb/ton)				
	Uncontrolled	Controlled				Uncontrolled[d]	Controlled[e]			
		Multiple Cyclones	Scrubber	ESP	Baghouse		Multiple Cyclones[f]	Scrubber[g]	ESP[g]	Baghouse[f]
15	32	54	81	79	97	3.2A	1.08A	0.48A	0.064A	0.02A
10	23	29	71	67	92	2.3A	0.58A	0.42A	0.054A	0.02A
6	17	14	62	50	77	1.7A	0.28A	0.38A	0.024A	0.02A
2.5	6	3	51	29	53	0.6A	0.06A	0.3A	0.024A	0.01A
1.25	2	1	35	17	31	0.2A	0.02A	0.22A	0.01A	0.006A
1.00	2	1	31	14	25	0.2A	0.02A	0.18A	0.01A	0.006A
0.625	1	1	20	12	14	0.10A	0.02A	0.12A	0.01A	0.002A
TOTAL	100	100	100	100	100	10A	2A	0.6A	0.08A	0.02A

[a] Reference 33. Applicable Source Classification Codes are 1-01-002-02, 1-02-002-02, 1-03-002-06, 1-01-002-12, 1-02-002-12, and 1-03-002-16. To convert from lb/ton to kg/Mg, multiply by 0.5. Emission Factors are lb of pollutant per ton of coal combusted, as fired. ESP = Electrostatic precipitator.

[b] Expressed as aerodynamic equivalent diameter.

[c] A = coal ash weight percent, as fired. For example, if coal ash weight is 8.2%, then A = 8.2.

[d] EMISSION FACTOR RATING = C.

[e] Estimated control efficiency for multiple cyclones is 80%; for scrubber, 94%; for ESP, 99.2%; and for baghouse, 99.8%.

[f] EMISSION FACTOR RATING = E.

[g] EMISSION FACTOR RATING = D.

Table 1.1-7. CUMULATIVE PARTICLE SIZE DISTRIBUTION AND SIZE-SPECIFIC EMISSION FACTORS FOR WET BOTTOM BOILERS BURNING PULVERIZED BITUMINOUS COAL[a]

EMISSION FACTOR RATING: E

Particle Size[b] (μm)	Cumulative Mass % ≤ Stated Size			Cumulative Emission Factor[c] (lb/ton)		
	Uncontrolled	Controlled		Uncontrolled	Controlled[d]	
		Multiple Cyclones	ESP		Multiple Cyclones	ESP
15	40	99	83	2.8A	1.38A	0.046A
10	37	93	75	2.6A	1.3A	0.042A
6	33	84	63	2.32A	1.18A	0.036A
2.5	21	61	40	1.48A	0.86A	0.022A
1.25	6	31	17	0.42A	0.44A	0.01A
1.00	4	19	8	0.28A	0.26A	0.004A
0.625	2	—[e]	—[e]	0.14A	—[e]	—[e]
TOTAL	100	100	100	7.0A	1.4A	0.056A

[a] Reference 33. Applicable Source Classification Codes are 1-01-002-01, 1-02-002-01, and 1-03-002-05. To convert from lb/ton to kg/Mg, multiply by 0.5. Emission factors are lb of pollutant per ton of coal combusted as fired. ESP = Electrostatic precipitator.

[b] Expressed as aerodynamic equivalent diameter.

[c] A = coal ash weight %, as fired. For example, if coal ash weight is 2.4%, then A = 2.4.

[d] Estimated control efficiency for multiple cyclones is 94%, and for ESPs, 99.2%.

[e] Insufficient data.

Table 1.1-8. CUMULATIVE SIZE DISTRIBUTION AND SIZE-SPECIFIC EMISSION FACTORS FOR CYCLONE FURNACES BURNING BITUMINOUS COAL[a]

EMISSION FACTOR RATING: E

Particle Size[b] (μm)	Cumulative Mass % ≤ Stated Size			Cumulative Emission Factor[c] (lb/ton)		
	Uncontrolled	Controlled		Uncontrolled	Controlled[d]	
		Multiple Cyclones	ESP		Multiple Cyclones	ESP
15	33	95	90	0.66A	0.114A	0.013A
10	13	94	68	0.26A	0.112A	0.011A
6	8	93	56	0.16A	0.112A	0.009A
2.5	5.5	92	36	0.11A[e]	0.11A	0.006A
1.25	5	85	22	0.10A[e]	0.10A	0.004A
1.00	5	82	17	0.10A[e]	0.10A	0.003A
0.625	0	—[f]	—[f]	0	—[f]	—[f]
TOTAL	100	100	100	2A	0.12A	0.016A

[a] Reference 33. Applicable Source Classification Codes are 1-01-002-03, 1-02-002-03, and 1-03-002-03. To convert from lb/ton to kg/Mg, multiply by 0.5. Emissions are lb of pollutant per ton of coal combusted, as fired.

[b] Expressed as aerodynamic equivalent diameter.

[c] A = coal ash weight %, as fired. For example, if coal ash weight is 2.4%, then A = 2.4.

[d] Estimated control efficiency for multiple cyclones is 94%, and for ESPs, 99.2%.

[e] These values are estimates based on data from controlled source.

[f] Insufficient data.

Table 1.1-9. CUMULATIVE PARTICLE SIZE DISTRIBUTION AND SIZE-SPECIFIC EMISSION FACTORS FOR SPREADER STOKERS BURNING BITUMINOUS COAL[a]

Particle Size[b] (μm)	Cumulative Mass % ≤ Stated Size					Cumulative Emission Factor (lb/ton)				
	Uncontrolled	Controlled				Uncontrolled[e]	Controlled			
		Multiple Cyclones[c]	Multiple Cyclones[d]	ESP	Baghouse		Multiple Cyclones[c,f]	Multiple Cyclones[d,e]	ESP[f,g]	Baghouse[e,g]
15	28	86	74	97	72	18.5	14.6	8.8	0.46	0.086
10	20	73	65	90	60	13.2	12	7.8	0.44	0.072
6	14	51	52	82	46	9.2	8.6	6.2	0.40	0.056
2.5	7	8	27	61	26	4.6	1.4	3.2	0.30	0.032
1.25	5	2	16	46	18	3.3	0.4	2.0	0.22	0.022
1.00	5	2	14	41	15	3.3	0.4	1.6	0.20	0.018
0.625	4	1	9	**C**[h]	7	2.6	0.2	1.0	**C**[h]	0.006
TOTAL	100	100	100	100	100	66.0	17.0	12.0	0.48	0.12

[a] Reference 33. Applicable Source Classification Codes are 1-01-002-04, 1-02-002-04, 1-03-002-09. To convert from lb/ton to kg/Mg, multiply by 0.5. Emissions are lb of pollutant per ton of coal combusted, as fired.

[b] Expressed as aerodynamic equivalent diameter.

[c] With flyash reinjection.

[d] Without flyash reinjection.

[e] EMISSION FACTOR RATING = C.

[f] EMISSION FACTOR RATING = E.

[g] Estimated control efficiency for ESP is 99.22%; and for baghouse, 99.8%.

[h] Insufficient data.

Table 1.1-10. CUMULATIVE PARTICLE SIZE DISTRIBUTION AND SIZE-SPECIFIC EMISSION FACTORS FOR OVERFEED STOKERS BURNING BITUMINOUS COAL[a]

Particle Size[b] (μm)	Cumulative Mass % ≤ Stated Size		Cumulative Emission Factor (lb/ton)			
			Uncontrolled		Multiple Cyclones Controlled[c]	
	Uncontrolled	Multiple Cyclones Controlled	Emission Factor	EMISSION FACTOR RATING	Emission Factor	EMISSION FACTOR RATING
15	49	60	7.8	C	5.4	E
10	37	55	6.0	C	5.0	E
6	24	49	3.8	C	4.4	E
2.5	14	43	2.2	C	3.8	E
1.25	13	39	2.0	C	3.6	E
1.00	12	39	2.0	C	3.6	E
0.625	—[d]	16	—[d]	C	1.4	E
TOTAL	100	100	16.0	C	9.0	E

[a] Reference 33. Applicable Source Classification Codes are 1-01-002-05, 1-02-002-05, and 1-03-002-07. To convert from lb/ton to kg/Mg, multiply by 0.5. Emissions are lb of pollutant per ton of coal combusted, as fired.

[b] Expressed as aerodynamic equivalent diameter.

[c] Estimated control efficiency for multiple cyclones is 80%.

[d] Insufficient data.

Table 1.1-11. CUMULATIVE PARTICLE SIZE DISTRIBUTION AND SIZE-SPECIFIC EMISSION FACTORS FOR UNDERFEED STOKERS BURNING BITUMINOUS COAL[a]

EMISSION FACTOR RATING: C

Particle Size[b] (µm)	Cumulative Mass % ≤ Stated Size	Uncontrolled Cumulative Emission Factor[c] (lb/ton)
15	50	7.6
10	41	6.2
6	32	4.8
2.5	25	3.8
1.25	22	3.4
1.00	21	3.2
0.625	18	2.7
TOTAL	100	15.0

[a] Reference 33. Applicable Source Classification Codes are 1-02-002-06 and 1-03-002-08. To convert from lb/ton to kg/Mg, multiply by 0.5. Emission factors are lb of pollutant per ton of coal combusted, as fired.

[b] Expressed as aerodynamic equivalent diameter.

[c] May also be used for uncontrolled hand-fired units.

Table 1.1-12 EMISSION FACTORS FOR POLYCHLORINATED DIBENZO-P-DIOXINS AND POLYCHLORINATED DIBENZOFURANS FROM CONTROLLED BITUMINOUS AND SUBBITUMINOUS COAL COMBUSTION

Controls	FGD-SDA with FF[a]		ESP or FF[b]	
Congener	Emission Factor[c] (lb/ton)	EMISSION FACTOR RATING	Emission Factor[c] (lb/ton)	EMISSION FACTOR RATING
2,3,7,8-TCDD	No data	---	1.43E-11	E
Total TCDD	3.93E-10	E	9.28E-11	D
Total PeCDD	7.06E-10	E	4.47E-11	D
Total HxCDD	3.00E-09	E	2.87E-11	D
Total HpCDD	1.00E-08	E	8.34E-11	D
Total OCDD	2.87E-08	E	4.16E-10	D
Total PCDD[d]	4.28E-08	E	6.66E-10	D
2,3,7,8-TCDF	No data	---	5.10E-11	D
Total TCDF	2.49E-09	E	4.04E-10	D
Total PeCDF	4.84E-09	E	3.53E-10	D
Total HxCDF	1.27E-08	E	1.92E-10	D
Total HpCDF	4.39E-08	E	7.68E-11	D
Total OCDF	1.37E-07	E	6.63E-11	D
Total PCDF[d]	2.01E-07	E	1.09E-09	D
TOTAL PCDD/PCDF	2.44E-07	E	1.76E-09	D

[a] Reference 34. Factors apply to boilers equipped with both flue gas desulfurization spray dryer absorber (FGD-SDA) and a fabric filter (FF). SCCs = pulverized coal-fired, dry bottom boilers, 1-01-002-02/22, 1-02-002-02/22, and 1-03-002-06/22.

[b] References 35-37. Factors apply to boilers equipped with an electrostatic precipitator (ESP) or a fabric filter. SCCs = pulverized coal-fired, dry bottom boilers, 1-01-002-02/22, 1-02-002-02/22, 1-03-002-06/22; and, cyclone boilers, 1-01-002-03/23, 1-02-002-03/23, and 1-03-002-03/23.

[c] Emission factor should be applied to coal feed, as fired. To convert from lb/ton to kg/Mg, multiply by 0.5. Emissions are lb of pollutant per ton of coal combusted.

[d] Total PCDD is the sum of Total TCDD through Total OCDD. Total PCDF is the sum of Total TCDF through Total OCDF.

Table 1.1-13 EMISSION FACTORS FOR POLYNUCLEAR AROMATIC HYDROCARBONS (PAH) FROM CONTROLLED COAL COMBUSTION[a]

Pollutant	Emission Factor[b] (lb/ton)	EMISSION FACTOR RATING
Biphenyl	1.7E-06	D
Acenaphthene	5.1E-07	B
Acenaphthylene	2.5E-07	B
Anthracene	2.1E-07	B
Benzo(a)anthracene	8.0E-08	B
Benzo(a)pyrene	3.8E-08	D
Benzo(b,j,k)fluoranthene	1.1E-07	B
Benzo(g,h,i)perylene	2.7E-08	D
Chrysene	1.0E-07	C
Fluoranthene	7.1E-07	B
Fluorene	9.1E-07	B
Indeno(1,2,3-cd)pyrene	6.1E-08	C
Naphthalene	1.3E-05	C
Phenanthrene	2.7E-06	B
Pyrene	3.3E-07	B
5-Methyl chrysene	2.2E-08	D

[a] References 35-45. Factors were developed from emissions data from six sites firing bituminous coal, four sites firing subbituminous coal, and from one site firing lignite. Factors apply to boilers utilizing both wet limestone scrubbers or spray dryers with an electrostatic precipitator (ESP) or fabric filter (FF). The factors also apply to boilers utilizing only an ESP or FF. Bituminous/subbituminous SCCs = pulverized coal-fired dry bottom boilers, 1-01-002-02/22, 1-02-002-02/22, 1-03-002-06; pulverized coal, dry bottom, tangentially-fired boilers, 1-01-002-12/26, 1-02-002-12/26, 1-03-002-16/26; and, cyclone boilers, 1-01-002-03/23, 1-02-002-03/23, and 1-03-002-03/23.

[b] Emission factor should be applied to coal feed, as fired. To convert from lb/ton to kg/Mg, multiply by 0.5. Emissions are lb of pollutant per ton of coal combusted.

Table 1.1-14 EMISSION FACTORS FOR VARIOUS ORGANIC COMPOUNDS FROM CONTROLLED COAL COMBUSTION[a]

Pollutant[b]	Emission Factor[c] (lb/ton)	EMISSION FACTOR RATING
Acetaldehyde	5.7E-04	C
Acetophenone	1.5E-05	D
Acrolein	2.9E-04	D
Benzene	1.3E-03	A
Benzyl chloride	7.0E-04	D
Bis(2-ethylhexyl)phthalate (DEHP)	7.3E-05	D
Bromoform	3.9E-05	E
Carbon disulfide	1.3E-04	D
2-Chloroacetophenone	7.0E-06	E
Chlorobenzene	2.2E-05	D
Chloroform	5.9E-05	D
Cumene	5.3E-06	E
Cyanide	2.5E-03	D
2,4-Dinitrotoluene	2.8E-07	D
Dimethyl sulfate	4.8E-05	E
Ethyl benzene	9.4E-05	D
Ethyl chloride	4.2E-05	D
Ethylene dichloride	4.0E-05	E
Ethylene dibromide	1.2E-06	E
Formaldehyde	2.4E-04	A
Hexane	6.7E-05	D
Isophorone	5.8E-04	D
Methyl bromide	1.6E-04	D
Methyl chloride	5.3E-04	D
Methyl ethyl ketone	3.9E-04	D
Methyl hydrazine	1.7E-04	E
Methyl methacrylate	2.0E-05	E

Table 1.1-14 (cont.).

Pollutant[b]	Emission Factor[c] (lb/ton)	EMISSION FACTOR RATING
Methyl tert butyl ether	3.5E-05	E
Methylene chloride	2.9E-04	D
Phenol	1.6E-05	D
Propionaldehyde	3.8E-04	D
Tetrachloroethylene	4.3E-05	D
Toluene	2.4E-04	A
1,1,1-Trichloroethane	2.0E-05	E
Styrene	2.5E-05	D
Xylenes	3.7E-05	C
Vinyl acetate	7.6E-06	E

[a] References 35-53. Factors were developed from emissions data from ten sites firing bituminous coal, eight sites firing subbituminous coal, and from one site firing lignite. The emission factors are applicable to boilers using both wet limestone scrubbers or spray dryers and an electrostatic precipitator (ESP) or fabric filter (FF). In addition, the factors apply to boilers utilizing only an ESP or FF. SCCs = pulverized coal-fired, dry bottom boilers, 1-01-002-02/22, 1-02-002-02/22, 1-03-002-06/22; pulverized coal, dry bottom, tangentially-fired boilers, 1-01-002-12/26, 1-02-002-12/26, 1-03-002-16/26; cyclone boilers, 1-01-002-03/23, 1-02-002-03/23, 1-03-002-03/23; and, atmospheric fluidized bed combustors, circulating bed, 1-01-002-18/38, 1-02-002-18, and 1-03-002-18.

[b] Pollutants sampled for but not detected in any sampling run include: Carbon tetrachloride- 2 sites; 1,3-Dichloropropylene- 2 sites; N-nitrosodimethylamine- 2 sites; Ethylidene dichloride- 2 sites; Hexachlorobutadiene- 1 site; Hexachloroethane- 1 site; Propylene dichloride- 2 sites; 1,1,2,2-Tetrachloroethane- 2 sites; 1,1,2-Trichloroethane- 2 sites; Vinyl chloride- 2 sites; and, Hexachlorobenzene- 2 sites.

[c] Emission factor should be applied to coal feed, as fired. To convert from lb/ton to kg/Mg, multiply by 0.5.

Table 1.1-15. EMISSION FACTORS FOR HYDROGEN CHLORIDE (HCI) AND HYDROGEN FLUORIDE (HF) FROM COAL COMBUSTION[a]

EMISSION FACTOR RATING: B

		HCl	HF
Firing Configuration	SCC	Emission Factor (lb/ton)	Emission Factor (lb/ton)
PC-fired, dry bottom	1-01-002-02/22 1-02-002-02/22 1-03-002-06/22	1.2	0.15
PC-fired, dry bottom, tangential	1-01-002-12/26 1-02-002-12/26 1-03-002-16/26	1.2	0.15
PC-fired, wet bottom	1-01-002-01/21 1-02-002-01/21 1-03-002-05/21	1.2	0.15
Cyclone Furnace	1-01-002-03/23 1-02-002-03/23 1-03-002-03/23	1.2	0.15
Spreader Stoker	1-01-002-04/24 1-02-002-04/24 1-03-002-09/24	1.2	0.15
Overfeed Stoker	1-01-002-05/25 1-02-002-05/25 1-03-002-07/25	1.2	0.15
Underfeed Stoker	1-02-002-06 1-03-002-08	1.2	0.15
FBC, Bubbling Bed	1-01-002-17 1-02-002-17 1-03-002-17	1.2	0.15
FBC, Circulating Bed	1-01-002-18/38 1-02-002-18 1-03-002-18	1.2	0.15
Hand-fired	1-03-002-14	1.2	0.15

[a] Reference 54. The emission factors were developed from bituminous coal, subbituminous coal, and lignite emissions data. To convert from

Table 1.1-16. EMISSION FACTOR EQUATIONS FOR TRACE ELEMENTS FROM COAL COMBUSTION[a]

EMISSION FACTOR EQUATION RATING: A[b]

Pollutant	Emission Equation ($lb/10^{12}$ Btu)[c]
Antimony	$0.92 * (C/A * PM)^{0.63}$
Arsenic	$3.1 * (C/A * PM)^{0.85}$
Beryllium	$1.2 * (C/A * PM)^{1.1}$
Cadmium	$3.3 * (C/A * PM)^{0.5}$
Chromium	$3.7 * (C/A * PM)^{0.58}$
Cobalt	$1.7 * (C/A * PM)^{0.69}$
Lead	$3.4 * (C/A * PM)^{0.80}$
Manganese	$3.8 * (C/A * PM)^{0.60}$
Nickel	$4.4 * (C/A * PM)^{0.48}$

[a] Reference 55. The equations were developed from emissions data from bituminous coal combustion, subbituminous coal combustion, and from lignite combustion. The equations may be used to generate factors for both controlled and uncontrolled boilers. The emission factor equations are applicable to all typical firing configurations for electric generation (utility), industrial, and commercial/industrial boilers firing bituminous coal, subbituminous coal, and lignite. Thus, all SCCs for these boilers are assigned to the factors.

[b] AP-42 criteria for rating emission factors were used to rate the equations.

[c] The factors produced by the equations should be applied to heat input. To convert from $lb/10^{12}$ Btu to kg/joules, multiply by 4.31×10^{-16}.

C = concentration of metal in the coal, parts per million by weight (ppmwt).
A = weight fraction of ash in the coal. For example, 10% ash is 0.1 ash fraction.
PM = Site-specific emission factor for total particulate matter, $lb/10^6$ Btu.

Table 1.1-17. EMISSION FACTORS FOR TRACE ELEMENTS, POM, AND HCOH FROM UNCONTROLLED BITUMINOUS AND SUBBITUMINOUS COAL COMBUSTION[a]

EMISSION FACTOR RATING: E

Firing Configuration (SCC)	Emission Factor, lb/10^{12} Btu									
	As	Be	Cd	Cr	Pb[b]	Mn	Hg	Ni	POM	HCOH
Pulverized coal, configuration unknown (no SCC)	ND	ND	ND	1922	ND	ND	ND	ND	ND	112[c]
Pulverized coal, wet bottom (1-01-002-01/21, 1-02-002-01/21, 1-03-002-05/21)	538	81	44-70	1020-1570	507	808-2980	16	840-1290	ND	ND
Pulverized coal, dry bottom (1-01-002-02/22, 1-02-002-06/22, 1-03-002-06/22)	684	81	44.4	1250-1570	507	228-2980	16	1030-1290	2.08	ND
Pulverized coal, dry bottom, tangential (1-01-002-12/26, 1-02-002-12/26, 1-03-002-16/26)	ND	ND	ND	ND	ND	ND	ND	ND	2.4	ND
Cyclone furnace (1-01-002-03/23, 1-02-002-03/23, 1-03-002-03/23)	115	<81	28	212-1502	507	228-1300	16	174-1290	ND	ND
Stoker, configuration unknown (no SCC)	ND	73	ND	19-300	ND	2170	16	775-1290	ND	ND
Spreader stoker (1-01-002-04/24, 1-02-002-04/24, 1-03-002-09/24)	264-542	ND	21-43	942-1570	507	ND	ND	ND	ND	221[d]
Overfeed stoker, traveling grate (1-01-002-05/25, 1-02-002-05/25, 1-03-002-07/25)	542-1030	ND	43-82	ND	507	ND	ND	ND	ND	140[e]

[a] References 56-61. The emission factors in this table represent the ranges of factors reported in the literature. If only 1 data point was found, it is still reported in this table. To convert from lb/10^{12} Btu to pg/J, multiply by 0.43. SCC = Source Classification Code. ND = no data.

[b] Lead emission factors were taken directly from an EPA background document for support of the National Ambient Air Quality Standards.

[c] Based on 2 units; 133 x 10^6 Btu/hr and 1550 x 10^6 Btu/hr.

[d] Based on 1 unit; 59 x 10^6 Btu/hr.

Table 1.1-18 EMISSION FACTORS FOR TRACE METALS FROM CONTROLLED COAL COMBUSTION[a]

Pollutant	Emission Factor (lb/ton)[b]	EMISSION FACTOR RATING
Antimony	1.8E-05	A
Arsenic	4.1E-04	A
Beryllium	2.1E-05	A
Cadmium	5.1E-05	A
Chromium	2.6E-04	A
Chromium (VI)	7.9E-05	D
Cobalt	1.0E-04	A
Lead	4.2E-04	A
Magnesium	1.1E-02	A
Manganese	4.9E-04	A
Mercury	8.3E-05	A
Nickel	2.8E-04	A
Selenium	1.3E-03	A

[a] References 35-53, 62-70. The emission factors were developed from emissions data at eleven facilities firing bituminous coal, fifteen facilities firing subbituminous coal, and from two facilities firing lignite. The factors apply to boilers utilizing either venturi scrubbers, spray dryer absorbers, or wet limestone scrubbers with an electrostatic precipitator (ESP) or Fabric Filter (FF). In addition, the factors apply to boilers using only an ESP, FF, or venturi scrubber. SCCs = pulverized coal-fired, dry bottom boilers, 1-01-002-02/22, 1-02-002-02/22, 1-03-002-06/22; pulverized coal, dry bottom, tangentially-fired boilers, 1-01-002-12/26, 1-02-002-12/26, 1-03-002-16/26; cyclone boilers, 1-01-002-03/23, 1-02-002-03/23, 1-03-002-03/23; and, atmospheric fluidized bed combustors, circulating bed, 1-01-002-18/38, 1-02-002-18, and 1-03-002-18.

[b] Emission factor should be applied to coal feed, as fired. To convert from lb/ton to kg/Mg, multiply by 0.5.

Table 1.1-19. EMISSION FACTORS FOR CH_4, TNMOC, AND N_2O FROM BITUMINOUS AND SUBBITUMINOUS COAL COMBUSTION[a]

Firing Configuration	SCC	CH_4[b]		TNMOC[b,c]		N_2O[d]	
		Emission Factor (lb/ton)	EMISSION FACTOR RATING	Emission Factor (lb/ton)	EMISSION FACTOR RATING	Emission Factor (lb/ton)	EMISSION FACTOR RATING
PC-fired, dry bottom, wall fired	1-01-002-02/22 1-02-002-02/22 1-03-002-06/22	0.04	B	0.06	B	0.03	B
PC-fired, dry bottom, tangentially fired	1-01-002-12/26 1-02-002-12/26 1-03-002-16/26	0.04	B	0.06	B	0.08	B
PC-fired, wet bottom	1-01-002-01/21 1-02-002-01/21 1-03-002-05/21	0.05	B	0.04	B	0.08	E
Cyclone furnace	1-01-002-03/23 1-02-002-03/23 1-03-002-03/23	0.01	B	0.11	B	0.09[e]	E
Spreader stoker	1-01-002-04/24 1-02-002-04/24 1-03-002-09/24	0.06	B	0.05	B	0.04[f]	D
Spreader stoker, with multiple cyclones, and reinjection	1-01-002-04/24 1-02-002-04/24 1-03-002-09/24	0.06	B	0.05	B	0.04[f]	E
Spreader stoker, with multiple cyclones, no reinjection	1-01-002-04/24 1-02-002-04/24 1-03-002-09/24	0.06	B	0.05	B	0.04[f]	E

Table 1.1-19 (cont.).

Firing Configuration	SCC	CH_4[b] Emission Factor (lb/ton)	CH_4[b] EMISSION FACTOR RATING	TNMOC[b,c] Emission Factor (lb/ton)	TNMOC[b,c] EMISSION FACTOR RATING	N_2O[d] Emission Factor (lb/ton)	N_2O[d] EMISSION FACTOR RATING
Overfeed stoker[g]	1-01-002-05/25 1-02-002-05/25 1-03-002-07/25	0.06	B	0.05	B	0.04[f]	E
Overfeed stoker, with multiple cyclones[g]	1-01-002-05/25 1-02-002-05/25 1-03-002-07/25	0.06	B	0.05	B	0.04[f]	E
Underfeed stoker	1-02-002-06 1-03-002-08	0.8	B	1.3	B	0.04[f]	E
Underfeed stoker, with multiple cyclone	1-02-002-06 1-03-002-08	0.8	B	1.3	B	0.04[f]	E
Hand-fed units	1-03-002-14	5	E	10	E	0.04[f]	E
FBC, bubbling bed	1-01-002-17 1-02-002-17 1-03-002-17	0.06[h]	E	0.05[h]	E	3.5[h]	B
FBC, circulating bed	1-01-002-18 1-02-002-18 1-03-002-18	0.06	E	0.05	E	3.5	B

[a] Factors represent uncontrolled emissions unless otherwise specified and should be applied to coal feed, as fired. SCC = Source Classification Code. To convert from lb/ton to kg/Mg, multiply by 0.5.

[b] Reference 32. Nominal values achievable under normal operating conditions; values 1 or 2 orders of magnitude higher can occur when combustion is not complete.

[c] TNMOC are expressed as C_2 to C_{16} alkane equivalents (Reference 71). Because of limited data, the effects of firing configuration on TNMOC emission factors could not be distinguished. As a result, all data were averaged collectively to develop a single average emission factor for pulverized coal units, cyclones, spreaders, and overfeed stokers.

[d] References 14-15.

Table 1.1-20. DEFAULT CO_2 EMISSION FACTORS FOR U. S. COALS[a]

EMISSION FACTOR RATING: C

Coal Type	Average %C[b]	Conversion Factor[c]	Emission Factor[d] (lb/ton coal)
Subbituminous	66.3	72.6	4810
High-volatile bituminous	75.9	72.6	5510
Medium-volatile bituminous	83.2	72.6	6040
Low-volatile bituminous	86.1	72.6	6250

[a] This table should be used only when an ultimate analysis is not available. If the ultimate analysis is available, CO_2 emissions should be calculated by multiplying the %carbon (%C) by 72.6 This resultant factor would receive a quality rating of "B".

[b] An average of the values given in References 2,76-77. Each of these references listed average carbon contents for each coal type (dry basis) based on extensive sampling of U.S. coals.

[c] Based on the following equation:

$$\frac{44 \text{ ton } CO_2}{12 \text{ ton C}} \times 0.99 \times 2000 \frac{\text{lb } CO_2}{\text{ton } CO_2} \times \frac{1}{100\%} = 72.6 \frac{\text{lb } CO_2}{\text{ton \%C}}$$

Where:

44 = molecular weight of CO_2,
12 = molecular weight of carbon, and
0.99 = fraction of fuel oxidized during combustion (Reference 16).

[d] To convert from lb/ton to kg/Mg, multiply by 0.5.

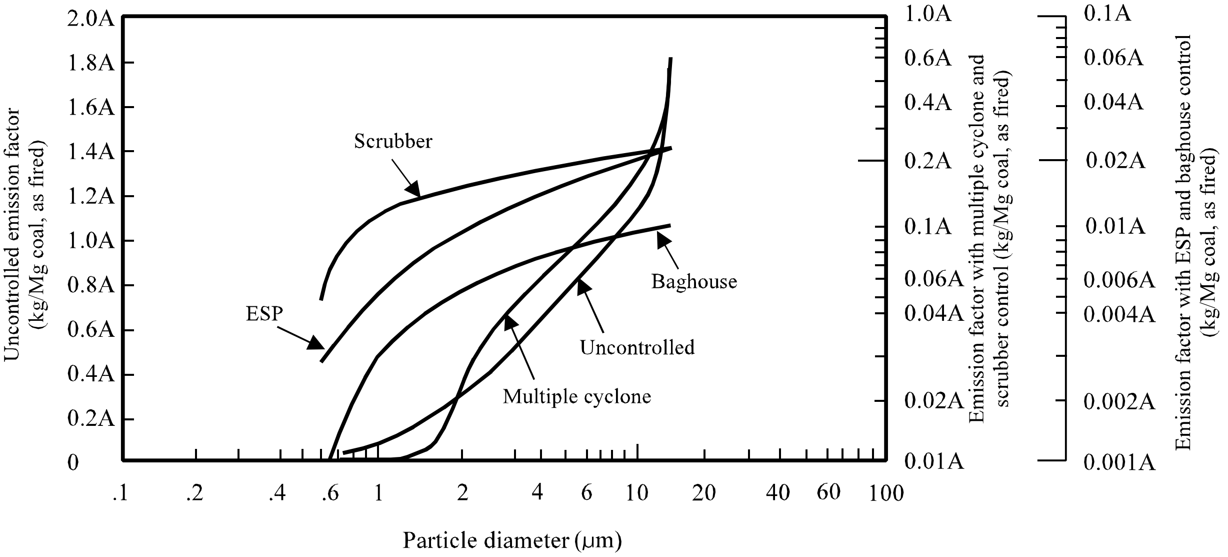

Figure 1.1-1. Cumulative size-specific emission factors for an example dry bottom boiler burning pulverized bituminous coal.

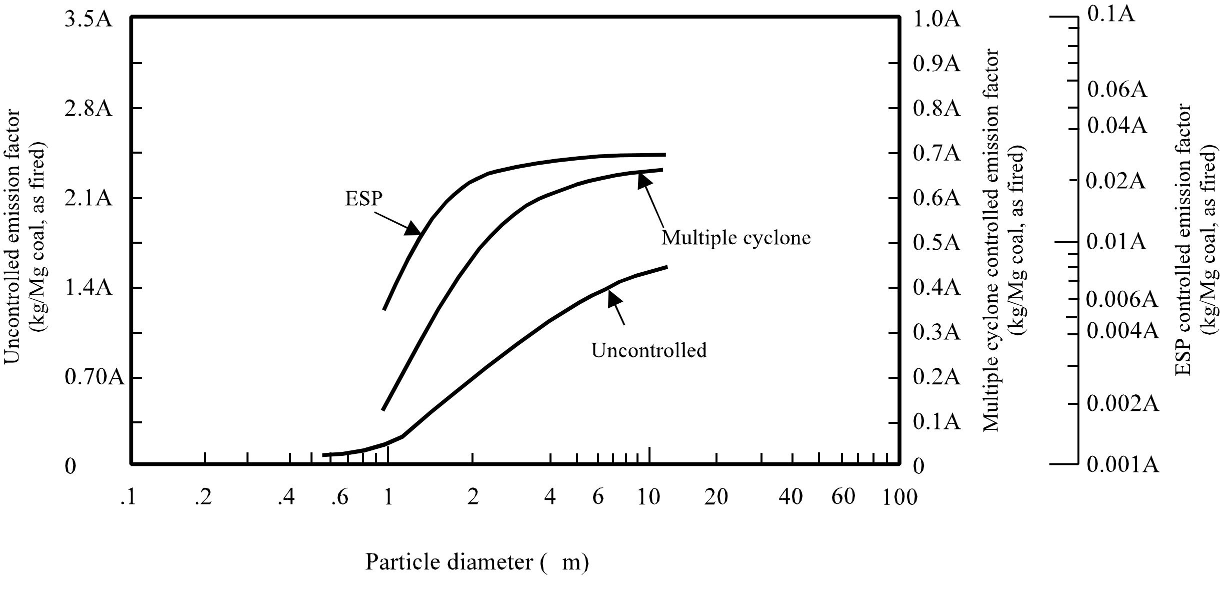

Figure 1.1-2. Cumulative size-specific emission factors for an example wet bottom boiler burning pulverized bituminous coal.

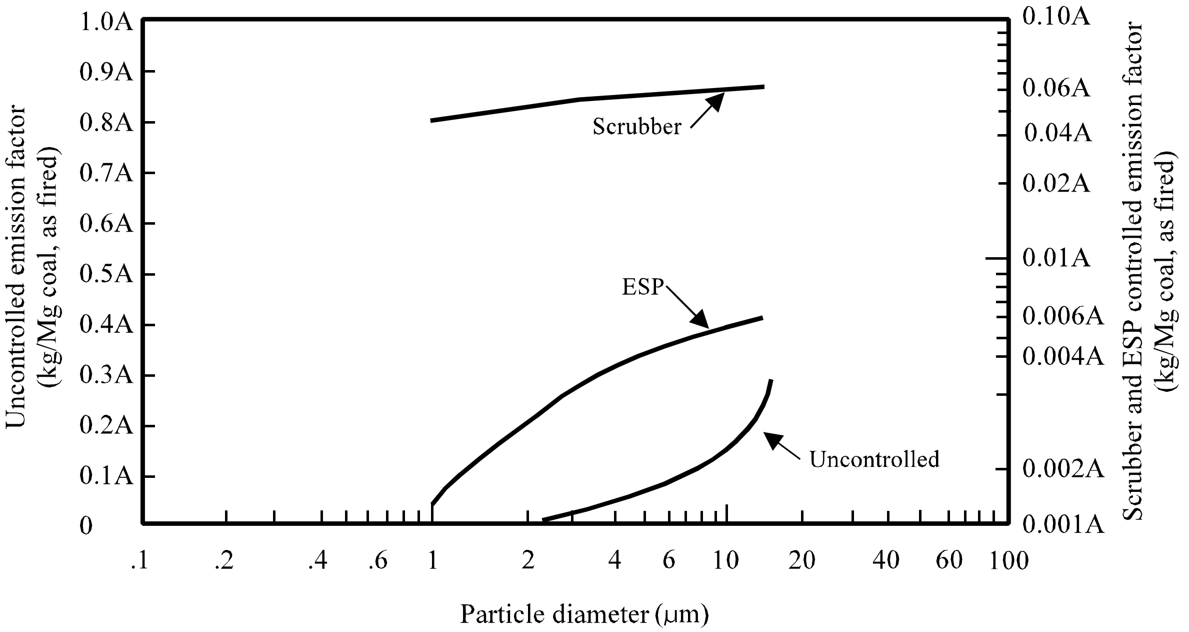

Figure 1.1-3. Cumulative size-specific emission factors for an example cyclone furnace burning bituminous coal.

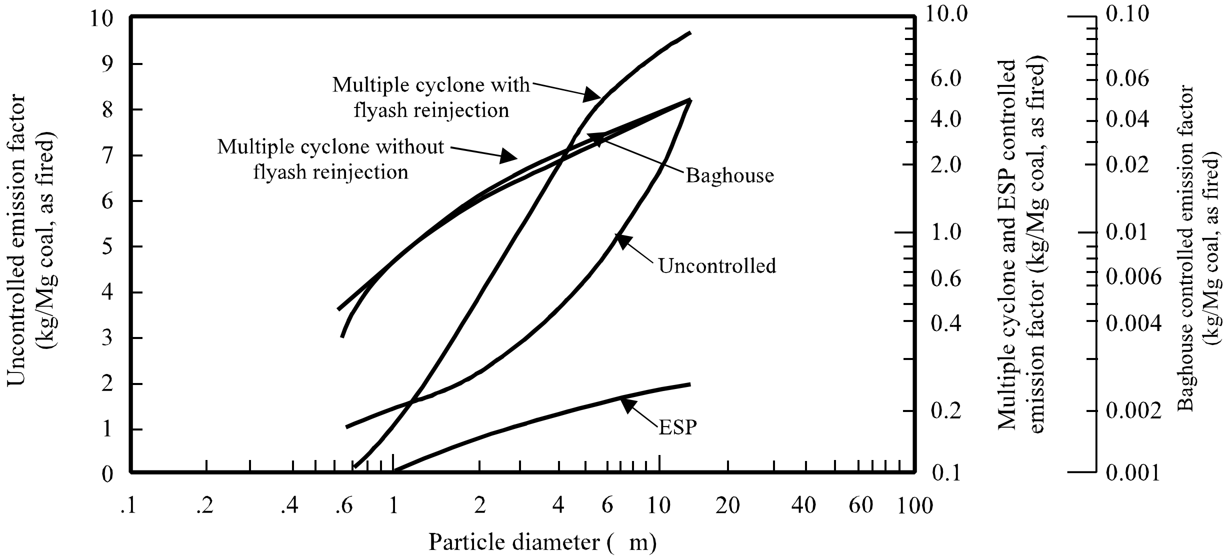

Figure 1.1-4. Cumulative size-specific emission factors for an example spreader stoker burning bituminous coal.

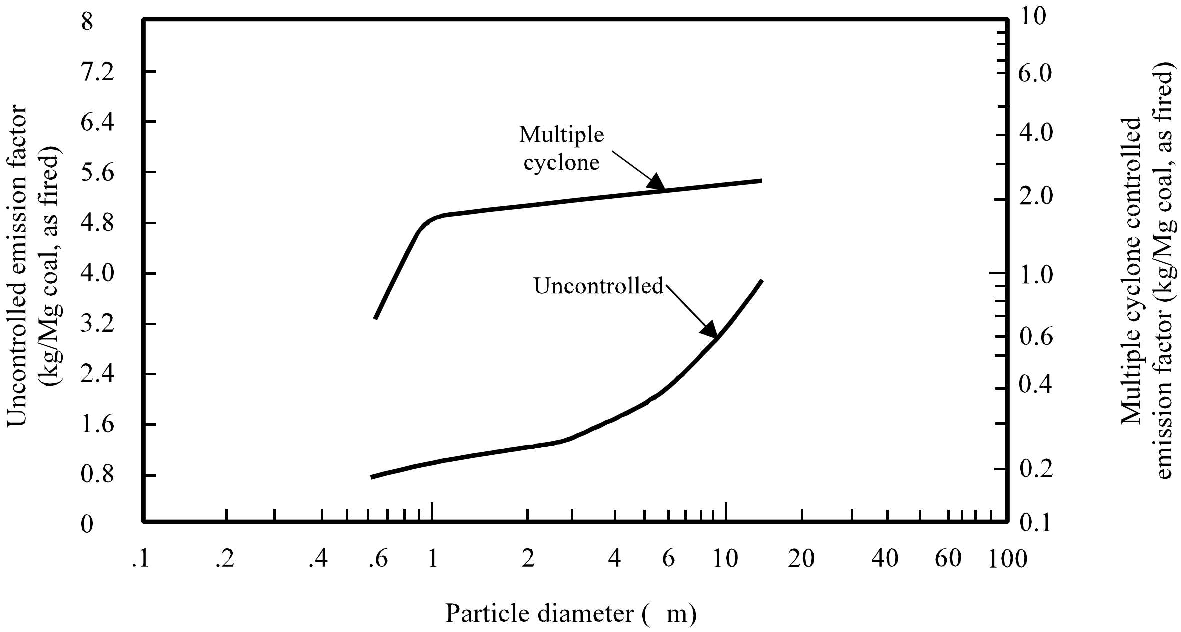

Figure 1.1-5. Cumulative size-specific emission factors for an example overfeed stoker burning bituminous coal.

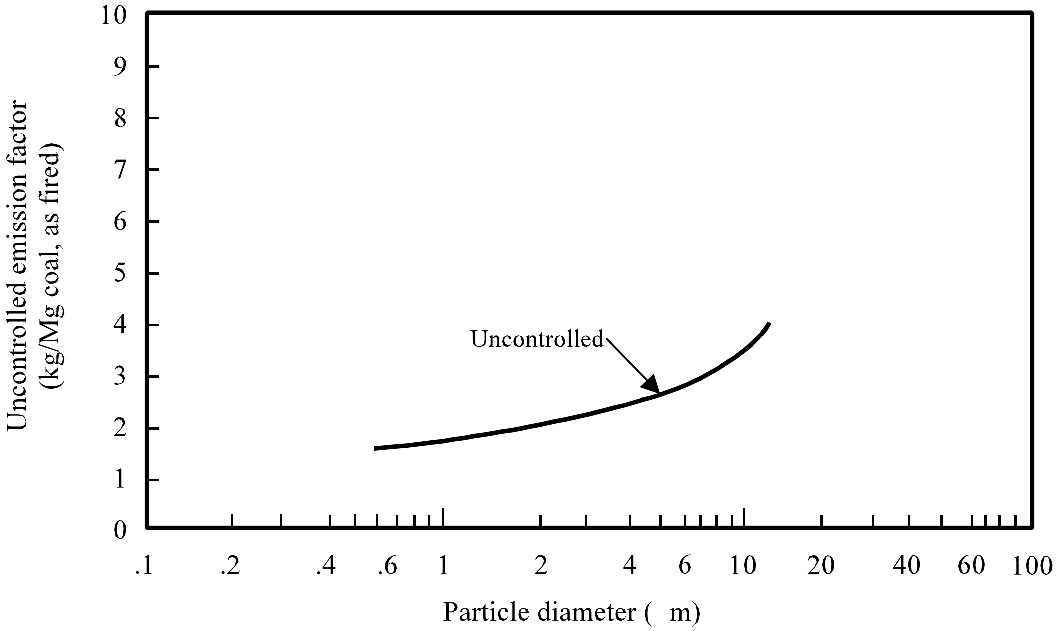

Figure 1.1-6. Cumulative size-specific emission factors for an example underfeed stoker burning bituminous coal.

References For Section 1.1

1. Bartok, B., Sarofina, A. F. (eds), *Fossil Fuel Combustion, A Source Book*, John Wiley & Sons, Inc., 1991, p. 239.

2. *Steam: It Generation And Use*, 38th Edition, Babcock and Wilcox, New York, 1975.

3. *Combustion*. Fossil Power Systems. Third Edition. Published by Combustion Engineering, Inc. Windsor, CT., 1981.

4. *Emission Factor Documentation For AP-42 Section 1.1 — Bituminous and Subbituminous Coal Combustiont*, U. S. Environmental Protection Agency, Research Triangle Park, NC, April 1993.

5. *Control Techniques For Nitrogen Oxides Emissions From Stationary Sources*, 2nd Edition, EPA-450/1-78-001, U. S. Environmental Protection Agency, Research Triangle Park, NC, January 1978.

6. *Review Of NO_x Emission Factors For Stationary Fossil Fuel Combustion Sources*, EPA-450/4-79-021, U. S. Environmental Protection Agency, Research Triangle Park, NC, September 1979.

7. K. J. Lim, *et al*., *Technology Assessment Report For Industrial Boiler Applications: NO_x Combustion Modification*, EPA-600/7-79-178f, U. S. Environmental Protection Agency, Research Triangle Park, NC, December 1979.

8. Particulate Polycyclic Organic Matter, National Academy of Sciences, Washington, DC, 1972.

9. Vapor Phase Organic Pollutants- Volatile Hydrocarbons and Oxidation Products, National Academy of Sciences, Washington, DC, 1976.

10. D. H. Klein, *et al*., "Pathways of Thirty-Seven Trace Elements Through Coal-Fired Power Plants", Environmental Science and Technology, 9:973-979,1975.

11. D. G. Coles, *et al*., "Chemical Studies of Stack Fly Ash from a Coal-Fired Power Plant", Environmental Science and Technology, 13:455-459, 1979.

12. S. Baig, *et al*., Conventional Combustion Environmental Assessment, EPA Contract No. 68-02-3138, U. S. Environmental Protection Agency, Research Triangle Park, NC, 1981.

13. L. P. Nelson, *et al*., *Global Combustion Sources of Nitrous Oxide Emissions*, Research Project 2333-4 Interim Report, Sacramento: Radian Corporation, 1991.

14. R. L. Peer, *et al*., *Characterization of Nitrous Oxide Emission Sources*, U. S. Environmental Protection Agency, Office of Research and Development, Research Triangle Park, NC, 1995.

15. S. D. Piccot, *et al*., *Emissions and Cost Estimates for Globally Significant Anthropogenic Combustion Sources of NO_x, N_2O, CH_4, CO, and CO_2*, U. S. Environmental Protection Agency, Office of Research and Development, Research Triangle Park, NC, 1990.

16. G. Marland and R. M. Rotty, *Carbon Dioxide Emissions from Fossil Fuels: A Procedure For Estimation and Results For 1951-1981*, DOE/NBB-0036 TR-003, Carbon Dioxide Research Division, Office of Energy Research, U.S. Department of Energy, Oak Ridge, TN, 1983.

17. G. Marland and R. M. Rotty, *Carbon Dioxide Emissions from Fossil Fuels: A Procedure For Estimation and Results For 1950-1982, Tellus,* 36B: 232-261.

18. *Sector-Specific Issues and Reporting Methodologies Supporting the General Guidelines for the Voluntary Reporting of Greenhouse Gases under Section 1605(b) of the Energy Policy Act of 1992* (1994) DOE/PO-0028, Volume 2 of 3, U.S. Department of Energy.

19. *Control Techniques For Sulfur Dioxide Emissions From Stationary Sources, 2nd Edition*, EPA-450/3-81-004, U. S. Environmental Protection Agency, Research Triangle Park, NC, April 1981.

20. *Alternative Control Techniques Document--*NO_x *Emissions From Utility Boilers,* EPA-453/R-94-023, March 1994, pp. 2-15, 2-18, 5-103.

21. *Emission Factor Documentation For AP-42, Section 1.1, Bituminous and Subbituminous Coal Combustion*, Prepared by Acurex Environmental Corp., Edward Aul & Associates, Inc., E. H. Pechan And Associates, Inc., EPA Contract No. 68-D0-11210, April 1993.

22. Carlo Castaldini, and Meredith Angwin, *Boiler Design And Operating Variables Affecting Uncontrolled Sulfur Emissions From Pulverized Coal Fired Steam Generators*, EPA-450/3-77-047, U. S. Environmental Protection Agency, Research Triangle Park, NC, December 1977.

23. K. Cushing, *et al*., "Fabric Filtration Experience Downstream From Atmospheric Fluidized Bed Combustion Boilers", Presented at the Ninth Particulate Control Symposium, October 1991.

24. Susan Stamey-Hall, *Evaluation of Nitrogen Oxide Emissions Data from TVA Coal-Fired Boilers,* EPA-600/R-92-242, U. S. Environmental Protection Agency, Research Triangle Park, NC, December 1992.

25. Joel Vatsky and Timothy W. Sweeney, *Development of an Ultra-Low* No_x *Pulverizer Coal Burner*, Presented at the EPA/EPRI 1991 Joint Symposium on Combustion No_x Control, March 25-28, 1991, Washington, DC.

26. T. L. Lu, R. L. Lungren, and A. Kokkinos, *Performance of a Large Cell-Burner Utility Boiler Retrofitted with Foster Wheeler Low-*NO_x *Burners*, Presented at the EPA/EPRI 1991 Joint Symposium on Combustion NO_x Control, March 25-28, 1991, Washington, DC.

27. *Alternative Control Techniques Document —* NO_x *Emissions from Utility Boilers*, EPA-453/R-94-023, U. S. Environmental Protection Agency, Research Triangle Park, NC, March 1994.

28. *Standards Of Performance For New Stationary Sources*, 36 FR 24876, December 23, 1971.

29. *Field Tests Of Industrial Stoker Coal Fired Boilers For Emission Control And Efficiency Improvement - Sites L1 — 17*, EPA-600/7-81-020a, U. S. Environmental Protection Agency, Washington, DC, February 1981.

30. *Application Of Combustion Modifications To Control Pollutant Emissions From Industrial Boilers — Phase I,* EPA-650/2-74-078a, U. S. Environmental Protection Agency, Washington, DC, October 1974.

31. *Source Sampling Residential Fireplaces For Emission Factor Development*, EPA-50/3-6-010, U. S. Environmental Protection Agency, Research Triangle Park, NC, November 1875.

32. *Atmospheric Emissions From Coal Combustion: An Inventory Guide*, 999-AP-24, U. S. Environmental Protection Agency, Washington, DC, April 1966.

33. *Inhalable Particulate Source Category Report For External Combustion Sources,* EPA Contract No. 68-02-3156, Acurex Corporation, Mountain View, CA, January 1985.

34. Results of the March 28, 1990 Dioxin Emission Performance Test on Unit 3 at the NSP Sherco Plant in Becker, Minnesota. Interpoll Laboratories, Inc., Circle Pines, Minnesota. July 11, 1990.

35. Field Chemical Emissions Monitoring Project: Site 22 Emissions Report. Radian Corporation, Austin, Texas. February, 1994.

36. Toxics Assessment Report. Illinois Power Company. Baldwin Power Station- Unit 2. Baldwin, Illinois. Volumes I- Main Report. Roy F. Weston, Inc. West Chester, Pennsylvania. December, 1993.

37. Toxics Assessment Report. Minnesota Power Company Boswell Energy Center- Unit 2. Cohasset, Minnesota. Volume 1-Main Report. Roy F. Weston, Inc. West Chester, Pennsylvania. December, 1993. (EPRI Report)

38. Field Chemical Emissions Monitoring Project: Site 11 Emissions Monitoring. Radian Corporation, Austin, Texas. October, 1992. (EPRI Report)

39. Field Chemical Emissions Monitoring Project: Site 21 Emissions Monitoring. Radian Corporation, Austin, Texas. August, 1993. (EPRI Report)

40. Field Chemical Emissions Monitoring Project: Site 111 Emissions Report. Radian Corporation, Austin, Texas. May, 1993. (EPRI Report)

41. Field Chemical Emissions Monitoring Project: Site 115 Emissions Report. Radian Corporation, Austin, Texas. November, 1994. (EPRI Report)

42. Draft Final Report. A Study of Toxic Emissions from a Coal-Fired Power Plant-Niles Station No. 2. Volumes One, Two, and Three. Battelle, Columbus, Ohio. December 29, 1993.

43. Draft Final Report. A Study of Toxic Emissions from a Coal-Fired Power Plant Utilizing an ESP/Wet FGD System. Volumes One, Two, and Three. Battelle, Columbus, Ohio. December 1993.

44. Assessment of Toxic Emissions From a Coal Fired Power Plant Utilizing an ESP. Final Report-Revision 1. Energy and Environmental Research Corporation, Irvine, California. December 23, 1993.

45. 500-MW Demonstration of Advanced Wall-Fired Combustion Techniques for the Reduction of Nitrogen Oxide (NOx) Emissions from Coal-Fired Boilers. Radian Corporation, Austin, Texas.

46. Results of the November 7, 1991 Air Toxic Emission Study on the Nos. 3, 4, 5 & 6 Boilers at the NSP High Bridge Plant. Interpoll Laboratories, Inc., Circle Pines, Minnesota. January 3, 1992.

47. Results of the December 1991 Air Toxic Emission Study on Units 6 & 7 at the NSP Riverside Plant. Interpoll Laboratories, Inc., Circle Pines, Minnesota. February 28, 1992.

48. Field Chemical Emissions Monitoring Project: Site 10 Emissions Monitoring. Radian Corporation, Austin, Texas. October, 1992. (EPRI Report)

49. Field Chemical Emissions Monitoring Project: Site 12 Emissions Monitoring. Radian Corporation, Austin, Texas. November, 1992. (EPRI Report)

50. Field Chemical Emissions Monitoring Project: Site 15 Emissions Monitoring. Radian Corporation, Austin, Texas. October, 1992. (EPRI Report)

51. Field Chemical Emissions Monitoring Project: Site 101 Emissions Report. Radian Corporation, Austin, Texas. October, 1994. (EPRI Report)

52. Field Chemical Emissions Monitoring Project: Site 114 Report. Radian Corporation, Austin, Texas. May, 1994. (EPRI Report)

53. Field Chemical Emissions Monitoring Report: Site 122. Final Report, Task 1 Third Draft. EPRI RP9028-10. Southern Research Institute, Birmingham, Alabama. May, 1995. (EPRI Report)

54. *Hydrogen Chloride And Hydrogen Fluoride Emission Factors For The NAPAP Inventory,* EPA-600/7-85-041, U. S. Environmental Protection Agency, October 1985.

55. *Electric Utility Trace Substances Synthesis Report, Volume 1,* Report TR-104614, Electric Power Research Institute, Palo Alto, CA, November 1994.

56. *Locating And Estimating Air Emissions From Sources Of Chromium*, EPA-450/4-84-007g, U. S. Environmental Protection Agency, July 1984.

57. *Locating And Estimating Air Emissions From Sources Of Formaldehyde,* (Revised), EPA-450/4-91-012, U. S. Environmental Protection Agency, March 1991.

58. *Estimating Air Toxics Emissions From Coal And Oil Combustion Sources*, EPA-450/2-89-001, Radian Corporation, Project Officer: Dallas W. Safriet, Research Triangle Park, NC, April 1989.

59. *Canadian Coal-Fired Plants, Phase I: Final Report And Appendices*, Report for the Canadian Electrical Association, R&D, Montreal, Quebec, Contract Number 001G194, Report by Battelle, Pacific Northwest Laboratories, Richland, WA.

60. R. Meij, Auteru dr., *The Fate Of Trace Elements At Coal-Fired Plants*, Report No. 2561-MOC 92-3641, Rapport te bestellen bij; bibliotheek N.V. KEMA, February 13, 1992.

61. *Locating And Estimating Air Emissions From Sources Of Manganese*, EPA-450/4-84-007h, September 1985.

62. Results of the September 10 and 11, 1991 Mercury Removal Tests on the Units 1 & 2, and Unit 3 Scrubber Systems at the NSP Sherco Plant in Becker, Minnesota. Interpoll Laboratories, Inc., Circle Pines, Minnesota. October 30, 1991.

63. Results of the November 5, 1991 Air Toxic Emission Study on the No. 1, 3 & 4 Boilers at the NSP Black Dog Plant. Interpoll Laboratories, Inc., Circle Pines, Minnesota. January 3, 1992.

64. Results of the January 1992 Air Toxic Emission Study on the No. 2 Boiler at the NSP Black Dog Plant. Interpoll Laboratories, Inc., Circle Pines, Minnesota. May 4, 1992.

65. Results of the May 29, 1990 Trace Metal Characterization Study on Units 1 and 2 at the Sherburne County Generating Station in Becker, Minnesota. Interpoll Laboratories, Inc., Circle Pines, Minnesota. July, 1990.

66. Results of the May 1, 1990 Trace Metal Characterization Study on Units 1 and 2 at the Sherburne County Generating Station. Interpoll Laboratories, Inc., Circle Pines, Minnesota. July 18, 1990.

67. Results of the March 1990 Trace Metal Characterization Study on Unit 3 at the Sherburne County Generating Station. Interpoll Laboratories, Circle Pines, Minnesota. June 7, 1990.

68. Field Chemical Emissions Monitoring Project: Site 19 Emissions Monitoring. Radian Corporation, Austin, Texas. April, 1993. (EPRI Report)

69. Field Chemical Emissions Monitoring Project: Site 20 Emissions Monitoring. Radian Corporation, Austin, Texas. March, 1994. (EPRI Report)

70. Characterizing Toxic Emissions from a Coal-Fired Power Plant Demonstrating the AFGD ICCT Project and a Plant Utilizing a Dry Scrubber /Baghhouse System. Final Draft Report. Springerville Generating Station Unit No. 2. Southern Research Insititute, Birmingham, Alabama. December, 1993.

71. *Emissions Of Reactive Volatile Organic Compounds From Utility Boilers*, EPA-600/7-80-111, U. S. Environmental Protection Agency, Washington, DC, May 1980.

72. *EPA/IFP European Workshop On The Emission Of Nitrous Oxide For Fuel Combustion*, EPA Contract No. 68-02-4701, Ruiel-Malmaison, France, June 1-2, 1988.

73. R. Clayton, *et al*., *NO_x Field Study*, EPA-600/2-89-006, U. S. Environmental Protection Agency, Research Triangle Park, NC, February 1989.

74. L. E. Amand, and S. Anderson, "Emissions of Nitrous Oxide from Fluidized Bed Boilers", Presented at the Tenth International Conference on Fluidized Bed Combustor, San Francisco, CA, 1989.

75. *Alternative Control Techniques Document--NO_x Emissions From Utility Boilers*, EPA-453/R-94-023, Office of Air Quality Standards, Research Triangle Park, NC, 1994.

76. Alliance Technologies Corporation, *Evaluation of Significant Anthropogenic Sources of Radiatively Important Trace Gases*, U. S. Environmental Protection Agency, Office of Research and Development, Research Triangle Park, NC, 1990.

77. R. A. Winschel, Richard, "The Relationship of Carbon Dioxide Emissions with Coal Rank and Sulfur Content," *Journal of the Air and Waste Management Association*, Vol. 40, no. 6, pp. 861-865, June 1990.

78. Public Service Electric and Gas Company Mercer Generating Station Unit No. 2 Emission Compliance Test Program. November 1994.

79. Particulate Emission Study Performed for Madison Gas and Electric Company at the Blount Street Station Units 7, 8, 9 Inlets/Outlets. Mostardi-Platt Associates, Inc. December 6, 1994.

80. Particulate Emission Study Performed for Marshfield Electric and Water Department at the Wildwood Station Marshfield Wisconsin Boiler 5 Stack. Mostardi-Platt Associates, Inc. January 23-25, 1990.

81. Report on Particulate, SO_2, and NO_x Compliance Testing. Dairyland Power Cooperative J.P. Madgett Stack. Alma, Wisconsin. CAE. January 6, 1995.

82. Particulate Emissions Test Results. Portland General Electric Coal-fired Power Plant. Boardman, Oregon. SAIC, Inc. January 25, 1994.

83. Report on Compliance Testing Performed at Marshfield Electric and Water Department Wildwood Station Unit 5, Marshfield, Wisconsin. Clean Air Engineering, December 11, 1989.

84. Portland General Electric Company Boardman Coal Plant. Unit #1 Coal-fired Boiler. Boardman, Oregon. August 24-27,1995.

85. Particulate Emission Compliance Study Performed for Portland General Electric at the Boardman Plant Unit 1 Stack. Boardman, Oregon. September 19, 1996.

86. Emissions Source Test Report. Portland General Electric Coal-Fired Power Plant. Boardman, Oregon. OMNI Environmental Services, Inc. October 17, 1990.

87. Source Emissions Test Report Compliance. Portland General Electric Coal-Fired Power Plant. Boardman, Oregon. OMNI Environmental Services. January 29, 1991.

88. Source Test Report. Particulate Emissions. Portland General Electric Coal-Fired Power Plant. Boardman, Oregon. OMNI Environmental Services, Inc. January 14, 1991.

89. Emissions Source Test Rpeort. Portland General Electric Coal-Fired Power Plant. Boardman, Oregon. OMNI Environmental Services, Inc. April 3, 1991.

90. Source Emissions Test Report. Portland General Electric Coal-Fired Power Plant. Boardman, Oregon. OMNI Environmental Services, Inc. January 21, 1992.

91. Particulate Emissions Test Results. Portland General Electric Coal-fired Power Plant. Boardman, Oregon. OMNI Environmental Services, Inc. April 4, 1992.

92. Particulate Emissions Test Results. Portland General Electric Coal-Fired Power Plant. Boardman, Oregon. OMNI Environmental Services, Inc. September 9, 1992.

93. Particulate Emissions Test Results. Portland General Electric Coal-Fired Power Plant. Boardman, Oregon. OMNI Environmental Services, Inc. November 6, 1992.

94. Particulate Emissions Test Results. Portland General Electric Coal-Fired Power Plant. Boardman, Oregon. OMNI Environmental Services, Inc. January 26, 1993.

95. Stationary Source Sampling Report. Keystone Cogeneration Facility. Keystone Cogeneration Facility. Logan Township, NJ. November 1994.

96. Source Emissions Survey of City Public Service Board J.K. Spruce Unit Number 1 Stack. METCO Environmental. December 1992.

97. Report of Particulate Emission Testing on the Number 1 Boiler at Associated Milk Products Incorporated Located in Jim Falls, Wisconsin. Environmental Services of American, Inc. November 1994.

98. Appletone Papers, Inc. Boiler Emission Test at Appleton, WI. May 11 and 12, 1993. Badger Laboratories and Engineering.

99. Appleton Papers, Inc. Boiler Emission Test Report at Appleton, WI. Badger Laboratories and Engineering. October 11, 1993.

100. Results of a Source Emission Compliance Test on Boiler #2 at the Hills Farm Heating Plant, Madison, Wisconsin. MMT Environmental Services, Inc. January 22, 1993.

101. Results of a Source Emission Compliance Test on Boiler #2 at the Hills Farm Heating Plant, Madison, Wisconsin. MMT Environmental Services, Inc. March 2, 1995.

102. Report to Mosinee Paper Company for Particulate Matter Emission Testing. No. 6 Boiler at Mosinee, Wisconsin. May 18, 19, and 20, 1993.

103. Report to Milwaukee County for Particulate Matter Emission Test Boiler No. 21. Environmental Technology and Engineering Corporation. November 5, 1991.

104. Report on Compliance Testing Conducted at Oscar Mayer Foods Corporation, Madison, Wisconsin. Clean Air Engineering. July 21, 1989.

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Combustion Aerosols: Factors Governing Their Size and Composition and Implications to Human Health

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ABSTRACT

Particulate matter (PM) emissions from stationary combustion sources burning coal, fuel oil, biomass, and waste, and PM from internal combustion (IC) engines burning gasoline and diesel, are a significant source of primary particles smaller than 2.5 µm ($PM_{2.5}$) in urban areas. Combustion-generated particles are generally smaller than geologically produced dust and have unique chemical composition and morphology. The fundamental processes affecting formation of combustion PM and the emission characteristics of important applications are reviewed. Particles containing transition metals, ultrafine particles, and soot are emphasized because these types of particles have been studied extensively, and their emissions are controlled by the fuel composition and the oxidant-temperature-mixing history from the flame to the stack. There is a need for better integration of the combustion, air pollution control, atmospheric chemistry, and inhalation health research communities. Epidemiology has demonstrated that susceptible individuals are being harmed by ambient PM. Particle surface area, number of ultrafine particles, bioavailable transition metals, polycyclic aromatic hydrocarbons (PAH), and other particle-bound organic compounds are suspected to be more important than particle mass in determining the effects of air pollution. Time- and size-resolved PM measurements are needed for testing mechanistic toxicological hypotheses, for characterizing the relationship between combustion operating conditions and transient emissions, and for source apportionment studies to develop air quality plans. Citations are provided to more specialized reviews, and the concluding comments make suggestions for further research.

INTRODUCTION

Combustion of coal, biomass, and petroleum-based fuels generates particulate matter (PM) ranging from millimeter-sized cinders and soot aggregates to ultrafine nuclei-mode primary particles only a few nanometers in diameter. The largest particles are removed in the combustion zone as bottom ash or wall deposits, or are collected in the post-combustion gas cleaning devices. The smaller particles travel with the combustion exhaust gas and contribute to ambient air pollution on both the urban and regional scale. Epidemiologic studies reported a correlation between adverse health effects and increases in ambient particulate concentration, even when the mass concentration was below the then-current air quality standards. This correlation motivated a call for stricter air quality regulations even though a toxicological mechanism linking small increases in ambient PM and biological responses is still unavailable. Particles smaller than 2.5 µm ($PM_{2.5}$) consist of the tail of the coarse-mode particle size distribution generated by mechanical processes and finer particles that are formed from gas-phase precursors by nucleation, condensation, and surface reaction on other particles, followed by particle growth from coagulation and other transformations in the atmosphere.

This review focuses on the submicron inorganic ash and soot produced by practical combustion systems because the processes by which these particles are produced have been extensively studied over the three decades since the passage of the U.S. Clean Air Act. Metal-enriched ash, soot, and ultrafine particles remain a concern for combustion researchers because these particles have been the focus of mechanistic toxicological hypotheses. Fundamental relationships are presented to show how the primary combustion particle size, morphology, and composition are determined by combustion conditions and the post-flame cool down. The implications of these fundamental relationships are illustrated by descriptions of the results of particle characterization studies from specific combustion applications. The relationships between the ability to measure particle characteristics, both at sources and in the atmosphere, the development of health effects hypotheses, and the development of regulations will be discussed. Examples illustrate recent progress and suggest areas for further work.

The epidemiology and toxicology of ambient PM is an active area of research. Recently, efforts in finding the causes of adverse health effects of particles have intensified.

Accumulating evidence suggests that mass concentration is not the most appropriate measure of potential health effects,[1] and that health studies need to consider other characteristics, such as particle number, particle morphology, and detailed chemical speciation.[2–4] The active toxicological hypotheses have been summarized into the following groups.[5] Some of these, such as mass, are listed based on the epidemiologic studies; others because there are known causal relations with health. There is no hierarchy to the listing.

(1) *PM Mass Concentration*. The initial epidemiologic studies correlated effects with mass as measured by ambient monitoring procedures. The mass concentration of individual chemical species in PM represents the maximum possible dose.

(2) *PM Particle Size/Surface Area*. Stronger associations are seen with fine particle mass, and the body interacts with the surface of an insoluble particle, not with the volume.

(3) *Ultrafine PM*. Particles smaller than 0.1 µm dominate the total number of particles in urban aerosols. Ultrafine particles are deposited deep in the lung by diffusion and can enter the body through the layer of cells lining the alveoli (air sacks) of the lung.

(4) *Metals*. Transition metals including Fe, V, Cu, and Ni act as catalysts in the formation of reactive oxygen species (ROS) and are associated with the activation of many biochemical processes.

(5) *Acids*. Inhalation studies have shown toxic responses that are associated with the amount of H^+ delivered to respiratory surfaces.

(6) *Organic Compounds*. Volatile and semi-volatile organic chemicals associated with particles can act as irritants and allergens. Many aromatic compounds are suspected mutagens or carcinogens and may have acute effects as well.

(7) *Biogenic Particles*. Pollen, spores, and proteins are known allergens. Ambient PM also includes viable bacteria and viruses, biologically generated toxins, and natural organic aerosols. Most pollen is larger than 10 µm, spores are typically 2–10 µm, bacteria are 0.5–20 µm, and viruses are submicron particles.

(8) *Salt and Secondary Aerosols*. Soluble salts formed by ocean spray and by gas-to-particle conversion are thought to be relatively benign. However, since secondary aerosols form a large part of the aerosol mass, the resulting particle mass is indirectly implicated by epidemiologic studies.

(9) *Peroxides*. Ambient peroxides associated with particles may be transported into the lung and may cause oxidant injury.

(10) *Soot*. Carbon black, a surrogate for elemental carbon (EC) in soot, causes tissue irritation and the release of toxic chemical intermediates from scavenger cells in laboratory studies. Soot particles also act as carriers for the organic compounds mentioned in hypothesis 6.

(11) *Cofactors*. The combination of two or more pollutants may cause greater or different effects than the individual pollutants acting separately.

Many of these particle classes or characteristics directly or indirectly involve combustion emissions. This review will emphasize particles containing transition metals, ultrafine particles, and soot because the formation of these types of particles during combustion can be explained by the oxidant-temperature-mixing history of the combustion and gas cleaning processes.

Figure 1 illustrates the main topics covered in this review. An overview of the fundamentals of particle formation in combustion, using coal combustion as a well-studied example, is followed by a discussion of the differences between the PM exiting the combustor and the emissions to the atmosphere. The PM emission characteristics from practical combustion applications, including chemical composition and size distribution, will be reviewed to identify sources of available data. The relationship between specific characteristics of combustion-generated particles and recent work in PM epidemiology, toxicology, and cell biology will be summarized to show the interaction between combustion engineering and the life sciences in addressing questions of public importance. Next, the current U.S. regulations regarding ambient PM will be discussed since the regulatory timetable is driving the need for parallel advances in both health- and engineering-related research. The particles emitted to the atmosphere differ from the particles created in combustion because of size-selective removal and other transformations in any air pollution control devices (APCDs), and examples will be given of studies that have integrated between the combustion and atmospheric emissions research communities. Finally, the need for advances in the ability to conduct time-, size-, and chemically-resolved investigations of fine particles both at combustion sources and in the ambient air will be discussed to illustrate how health studies, air pollution regulations, and control technology all depend on advances in what can be measured.

This paper will focus on the $PM_{2.5}$, PM_1, and ultrafine particles that are emitted as solids from mobile and stationary combustion sources. While combustion emissions of nitrogen and sulfur oxides are of importance from the standpoint of secondary particle formation (nitrates and sulfates), these gas-phase emissions and the subsequent atmospheric transformations will not be discussed. Post-combustion gas cleaning, atmospheric chemistry, and airway

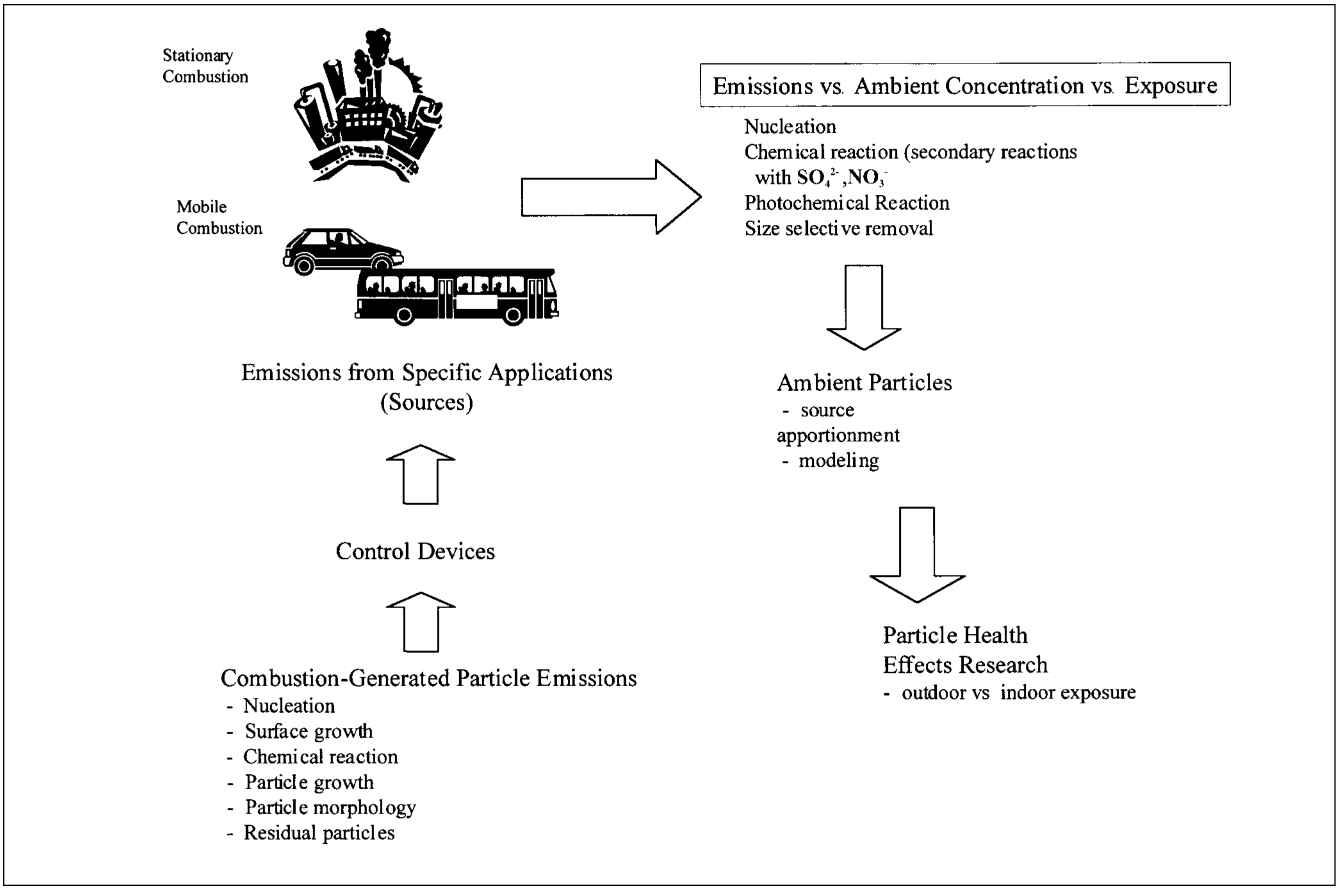
Stationary Combustion
Mobile Combustion
Emissions from Specific Applications (Sources)
Control Devices
Combustion-Generated Particle Emissions
- Nucleation
- Surface growth
- Chemical reaction
- Particle growth
- Particle morphology
- Residual particles
Emissions vs. Ambient Concentration vs. Exposure
Nucleation
Chemical reaction (secondary reactions with SO_4^{2-},NO_3^-
Photochemical Reaction
Size selective removal
Ambient Particles
- source apportionment
- modeling
Particle Health Effects Research
- outdoor vs indoor exposure

Figure 1. Roadmap to the particle formation and health effects topics discussed in this review.

deposition will also not be discussed in depth even though these processes all modify the characteristics of the aerosol as it travels between the combustion source and the site where the particles interact with the human body.

The following definitions are used in this paper: PM_{10}, $PM_{2.5}$, and PM_1 refer generically to particles with an aerodynamic diameter smaller than 10, 2.5, and 1 µm, respectively, and not specifically to the ambient particle mass as measured by federal reference test methods. Ultrafine particles refer to particles smaller than 0.1 µm, but it should be noted that the older literature occasionally used a larger size as the definition for ultrafine PM. Nanoparticles will refer to particles smaller than 0.01 µm (10 nm). Primary particles, as used in this paper, will be restricted to the roughly spherical structures of inorganic or carbonaceous condensation aerosols that make up aggregate particles. The term primary particles is also used in atmospheric PM research to refer to particles that are collected on filters at the source in contrast to secondary particles formed in the atmosphere from gas-phase precursors. Atmospheric chemistry references[6,7] cover secondary particle formation in detail. The term nuclei will be reserved for the nanometer-sized particles initially formed from gas-phase precursors. Accumulation mode will refer to the 0.1- to 1-µm particles that have long lifetimes in suspension because both diffusion and inertial removal mechanisms are slowest in this size range. The term nucleation mode, as used in the literature, often refers to transient concentrations of submicron particles, which are nuclei that have undergone significant additional growth by condensation and surface reaction. Depending on the context, these particles will be referred to either as a transient mode, to emphasize their rapid transformation, or as a condensation mode, to emphasize that they are derived from vapor-phase material and not from the solid or liquid residue of the fuel.

FUNDAMENTALS OF COMBUSTION-GENERATED PM

The combustion sources of ambient particles include stationary boilers and furnaces, stationary and mobile internal combustion (IC) engines, fugitive emissions from industrial processing, domestic fires, open burning, and accidental fires. The primary particles consist of inorganic or organic species, or a combination of the two. Combustion aerosols are multimodal. The finest particles are produced by gas-to-particle conversions and form the nuclei, or nanoparticles. These grow by coagulation and surface growth into the "accumulation" mode. The larger supermicron particles are produced from the inorganic material that remains in the solid or liquid phase with the fuel and is referred to as residual ash PM. The emissions depend on the composition of the fuels, the combustion conditions, and the effectiveness of any gas cleaning devices that are used. The emissions of each class of combustor are sufficiently different to merit separate coverage in this review. However, the principles governing their formation are sufficiently alike to warrant collective treatment in this introductory section.

The extensive literature on particle formation and emission, based on both laboratory and field studies, is summarized to show how operating and process conditions affect the size distribution and composition of combustion aerosols. The formation of fly ash from pulverized coal-fired and oil-fired boilers, toxic metal emissions from incinerators, and soot emissions from both stationary combustion and IC engines have been studied extensively and can serve as illustrative examples of the more general processes taking place in all flames. Other important combustion sources of particulate air pollution, such as domestic heating and open burning, are not well characterized compared with large boilers and furnaces or mass-produced engines.

Simplified quantitative relationships give mechanistic insights into the formation of the combustion aerosol under typical conditions. For sufficiently high initial particle number, the evolving size distribution of the submicron aerosol becomes independent of the number of particles nucleated, and the aerosol characteristics can be estimated from algebraic equations. The particle size distribution is determined by the volume fraction of the aerosol that is produced by initial nucleation and by subsequent coagulation and surface growth. Mass transfer limited surface growth can be predicted from the concentration of the condensing species. In multicomponent systems, the growth from condensation and surface reaction can be distinguished by the variation of chemical composition with particle size. The final particle morphology is determined by the ratio of time between collisions and the time for coalescence of the contacting particles.

Particle Inception

There are four classes of particles that form from gas or vapor precursors in combustion systems:

- inorganic particles produced at high temperatures,
- H_2SO_4 produced at exhaust temperatures,
- soot produced at high temperatures, and
- condensable organic particles produced at exhaust temperatures.

Three of these, inorganic ash particles, H_2SO_4 droplets, and condensable organics, involve homogeneous or heterogeneous nucleation. The total amount of condensation for these three categories is well defined, being approximately equal to the amount of initially vaporized material that is in excess of equilibrium at the ambient temperature. For soot, both the nucleation step and the amount of soot are determined by detailed kinetics rather than by thermodynamic equilibrium.

Particle Inception by Nucleation

The nucleation step involves the transformation of a vapor or liquid to clusters of the vapor "monomer" by a series of reversible steps. The clusters will persist and grow when the free energy change accompanying the phase transformation is negative. The fundamentals of nucleation are covered by Seinfeld and Pandis.[6] They discuss the dynamics of cluster formation and evaporation and the formation of critical size nuclei using both classical theory and more rigorous approaches. The critical size is the boundary between incipient particles that are stable and can continue to grow and unstable clusters that redisperse into the gas phase.

In combustion systems, the nuclei are expected to consist of clusters of relatively few atoms and to be of a size of tenths of nanometers. Due to the Kelvin effect,[8] the saturation vapor pressure increases as the particle size decreases, and extremely high supersaturation ratios are needed to make an organic liquid particle smaller than 10 nm stable. These high supersaturations can occur for EC and for refractory metal oxides. It is likely that much of the reported nucleation of condensable acid or organic aerosols in combustion systems actually involves the growth of inorganic ash or soot nuclei that are smaller than the detection limit of the available instruments, resulting in a sudden increase in measured particle number. The Kelvin effect assumes a continuum model and predicts that saturation pressure goes to infinity as the particle radius goes to zero. However, below a certain number of molecules, certain bulk properties, such as surface tension, are no longer applicable.

The classical theory, which assigns bulk properties to clusters, often predicts a critical nucleation size less than the size of a molecule.[9,10] The classical theory is of value in showing the tendency to nucleate, but not in providing the size of the nuclei. More rigorous approaches are available, such as using density function theory to calculate the free energy of clusters.[11,12] The nucleation steps in combustion will be complicated by the strong temperature and concentration profiles in a flame and surrounding individual burning particles. The calculations of the nucleation rate are further complicated by the mixtures of condensable compounds present in combustion products, since the favored nuclei will be multicomponent[13] and the presence of other particles can lead to heterogeneous nucleation.[6] Fortunately, as pointed out by Flagan and Friedlander,[14] since the time for the nucleation and growth of particles is small relative to the total residence time in a combustor, the details of the early nucleation steps will, in most cases, have little impact on the final number and size of the inorganic aerosols.

Nucleation versus Surface Growth

The competition between nucleation of new particles and surface growth is an issue whenever combustion products with condensable vapors are cooled in the presence of other aerosols. As the combustion products are cooled, the supersaturated vapors can either condense on the surfaces of existing particles or can form new nuclei. This problem was addressed for pulverized coal combustion by McNallan et al.,[15] who modeled the supersaturation versus time of gases cooling at various rates. They allowed for condensation on the surfaces of existing particles and particle formation according to classical nucleation theory. The criterion for nucleation was the development of the supersaturation partial pressure necessary to yield a nucleation rate of 1 particle/cm^3/sec. Assuming a pre-existing aerosol concentration of 1 g/m^3 of 8 μm particles, which approximates the residual fly ash encountered in pulverized coal combustion, and assuming an initial condition of silica vapors at equilibrium with pure silica at a temperature of 2400 K, they predicted that nucleation of silica vapors will occur at temperature of 2320 K for a cooling rate of 1000 K/sec, or at 2240 K for a cooling rate of 600 K/sec. Nucleation was not predicted to occur at 200 K/sec. They also examined the condensation of Na_2SO_4 and lead vapor and concluded that nucleation would not occur for these compounds in the presence of high-surface-area submicron particles. Cooling rates in the burner region of boilers are above 600 K/sec, so this simple analysis indicates that refractory oxides, such as SiO_2, will condense in the flame zone to produce a high surface area aerosol, which will prevent the subsequent nucleation of trace elements in the colder exhaust gases.

Experiments with pulverized coal in laboratory reactors show that nucleation occurs early in the flame zone for both soot and inorganic particles.[16–20] This is supported by simple treatments of nucleation and growth of particles in a boundary layer.[21–23] More detailed treatment of nucleation in the boundary layer of a growing particle is presented by Peshty et al.,[24] who show that the correct treatment should allow for heat release due to condensation, which tends to suppress the nucleation rate locally.

Temperatures decrease through the convection passes of a steam-generation boiler and on into the stack plume, and a point may be reached where H_2SO_4 is supersaturated. Again, there is the potential to form new particles by nucleation versus deposition on existing particles. This is a concern because H_2SO_4 deposited as a layer on coal fly ash has been shown to accentuate respiratory impairment.[25,26] H_2SO_4 condensation is an issue with both high-sulfur and low-sulfur coals because the deposition of H_2SO_4 on particles by SO_3 injection is used to control the resistivity of fly ash in electrostatic precipitators (ESPs).

Another situation where nucleation versus surface growth is important is H_2SO_4 condensation on soot or metal oxide nuclei and the formation of ultrafine particles in the exhaust of diesel engines. The condensation of the organics in diesel exhaust also has a major impact on the size distribution of PM emissions.[27] The effect of particle transformations during cool-down and dilution on reported size distributions will be discussed in the measurements section.

Particle (Soot) Inception by Chemical Reaction

Soot, unlike the inorganic oxide particles and condensable organic PM, is produced by a sequence of chemical reactions, some of which are essentially irreversible. The chemical reactions result in clusters of increasing molecular weight that grow into the measurable size range where the structures are considered particles. The smallest soot particles that have been observed by electron microscopy are in the range of 1–2 nm.[28,29] A soot particle with a diameter of 1.5 nm and a specific gravity of ~1.8 contains ~160 carbon atoms. For soot, particle inception is defined as the particles first capable of measurement, in contrast to the nucleation process where there is a critical particle size at which nucleation occurs for a particular supersaturation.

The vast literature on soot formation and oxidation has been summarized in various reviews and specialized conferences on soot.[30–35] Despite the large amount of literature on soot, the models of soot formation are still evolving. The three chemical kinetic components of a soot model are particle inception, surface growth, and surface oxidation. Coupled to the chemistry controlling the conversion of molecular precursors into solid soot are the physical models of particle coagulation and coalescence, which determine the soot structure.

Soot forms under fuel-rich conditions in which hydrocarbon fragments have a greater chance of colliding with other hydrocarbon fragments and growing, rather than being oxidized to CO, H_2, CO_2, and H_2O. At equilibrium, soot exists when C/O exceeds 1.0. Soot, however, is observed in flames of premixed hydrocarbons in air at C/O values of between 0.5 and 0.9.[32] In diffusion flames, soot forms even in the presence of excess air, since oxygen-deficient conditions will always be found on the fuel side of the flame front.

The reactions leading to soot are shown schematically in Figure 2, which is based on Bockhorn[30] and others. One of the critical steps in soot formation is the formation of the first aromatic ring, usually benzene. It is for this reason that fuels having a high aromatic hydrocarbon content form soot easily. This has been described in terms of a threshold sooting index for various classes of organic compounds.[36] Molecular weight growth then proceeds with the formation of polycyclic aromatic hydrocarbons (PAH), which are considered to be precursors to soot. The formation mechanisms proceed either through a sequence of hydrogen abstractions and acetylene addition or by the polymerization of the aromatic moieties that are produced.[37,38] Both mechanisms occur in parallel. Positive ions in the flame have been proposed as the initial nuclei sites for soot particle formation.[37,39]

Particle Growth by Collisions

Once particles are formed by either nucleation or chemical reactions, they will grow by a combination of coagulation and surface deposition. The consequences of coagulation will be treated in this section. For the following analysis, it is assumed that all the aerosol mass originates as n_0 particles of diameter d_0 at a time of zero and that the particles coalesce on each collision. The evolution of the particle diameter with time is readily obtained by applying the continuous coagulation equation[6]

$$\frac{dn(v,t)}{dt} = \frac{1}{2}\int_0^v K\,n(v-q,t)n(q,t)dq - n(v,t)\int_0^\infty K\,n(q,t)dq \qquad (1)$$

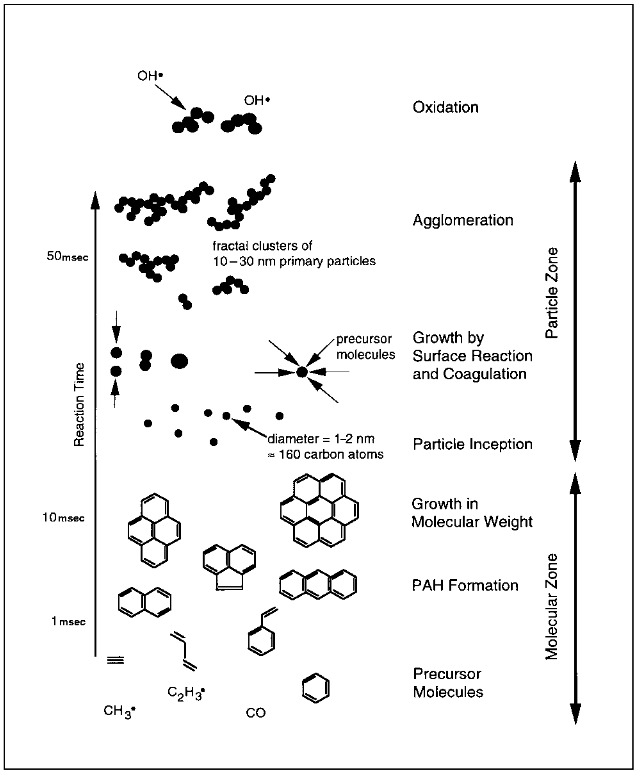

Figure 2. Kinetically limited chemical reactions and physical processes involved in soot formation. Based on Bockhorn.[30]

where $n(v,t)$ is the number of particles of volume v at time t, and K is the collision coefficient, which varies with particle size. Equation 1 is a simplification of the general dynamic equation[40] for the limiting case of no particle sources and no transport into the control volume. The first term in eq 1 corresponds to the production of particles of volume v by collisions of all combinations of smaller particles, $(v - q)$ and q. The second term is the loss of particles out of the size range by collisions with all other particles. This form of the aerosol dynamic equation assumes that the initial particle volume is vanishingly small compared to the system volume ($f_v \approx 0$). Expressions for K are available for the continuum, transition, and free molecular regimes, depending upon whether the particle size is much larger than, comparable to, or smaller than the mean free path of the ambient gas.[40,41]

MAEROS is a widely used numerical code for simulating multicomponent aerosol coagulation. MAEROS solves eq 1 by approximating the polydisperse aerosol with a series of constant size sections.[42] Sectional methods do not accurately model the behavior of the particle nuclei or molecular clusters. Discrete-sectional methods treat molecular clusters as discrete particles, then switch to a sectional approximation for larger particles.[43] Discrete-sectional codes are the most accurate method for numerically solving the aerosol dynamic equation over the entire size spectrum, but these methods are susceptible to problems with numerical diffusion, and care should be exercised in their use.[44] Analytical approximations for solving eq 1 for polydisperse coagulation have been developed by making simplifying approximations, such as by assuming a lognormal size distribution.[45,46] Other methods for calculating multicomponent aerosol dynamics have also been developed.[47–50]

For monodisperse aerosols, $n(v - q)$ is 0, and $n(v,t) = n(q,t) = n$, so eq 1 simplifies to

$$\frac{dn}{dt} = -Kn^2 \qquad (2)$$

The collision rate increases with the square of the particle number concentration and increases non-linearly with decreasing particle size, since K varies with particle size in the transition and free molecular regimes. This equation can be solved to obtain the decay in number concentration as function of time

$$n(v,t) = \frac{n_0}{1 + n_0 K t} \qquad (3)$$

The characteristic time scale for coagulation, assuming K is constant (valid in the continuum regime), is[51]

$$t_c = \frac{2}{Kn_0} \qquad (4)$$

For $n_0Kt >> 1$, the number of particles becomes independent of n_0, so the details of the initial nucleation rate are not needed to calculate the final aerosol distribution.[14] For a boiler with a residence time of 6 sec to the precipitator, the asymptotic relations will be valid for $n_0 > 10^9$ particles/cm^3. U.S. coals average an ash content of 10%. Typically, on the order of 1% of the ash vaporizes to produce the submicron fume. This yields values of n_0 on the order of 10^{14} particles/cm^3 for 1-nm particles and 10^{11} particles/cm^3 for 10-nm particles. Emission of 0.1% of the fuel as soot will give about the same values of n_0. The coagulation coefficient, K, varies with particle size and with gas temperature, so eq 3 is approximate. However, K varies by less than an order of magnitude over the 10-nm to 1-μm size range, and the initial nuclei number is orders of magnitude higher than that needed to make $n_0Kt > 1$. The limiting formulae will be a reasonable model for the submicron condensation aerosols formed by most stationary combustion systems.

In this limit, if the volume of aerosol formed per unit volume of space is f_v, then the particle diameter $d(t)$ is given by[40]

$$d(t) = \left(\frac{6 f_v K t}{\pi}\right)^{1/3} \qquad (5)$$

where K is a constant, given by $8kT/3\eta$, for particles in the continuum regime; k is the Boltzmann constant, and η is the gas viscosity.

For the free molecular or kinetic regime, K is a known function of the particle diameter and velocity. The equation for the rate of change in number density, for this case and a fixed f_v, is given by[33]

$$\frac{dn}{dt} = -\frac{6}{5} k_t f_v^{1/6} n^{11/6} \qquad (6)$$

where

$$k_t = \frac{5}{12}\left(\frac{3}{4\pi}\right)^{1/6}\left(\frac{6kT}{\rho}\right)^{1/2} G\alpha \qquad (7)$$

and ρ is particle density; G is the enhancement factor to allow for the van der Waals acceleration factor that is a function of the Hamaker constant,[8,52] and it has a value of about 2; and α is a factor to allow for the particle size distribution, and it has a value of 5.66 for monodisperse particles. The exponent of n of 11/6 in eq 6 versus the exponent of 2 in eq 2 is a consequence of allowing for the dependence of collision rate with particle size and the constraint that f_v is constant.

Friedlander and co-workers showed that, if allowance is made for the polydisperse particles, a self-preserving size distribution is approached.[40,53] For this case, the particles have a narrow size distribution with a geometric standard deviation of 1.37 for the diameter, and the coefficient α has a value of 6.55, not very different from the value of 5.66 for a monodisperse aerosol. Solution of eq 6 for a fixed volume fraction of aerosols f_v then yields the following relations for particle number and particle size:

$$n(t) = \left(k_t f_v^{1/6} t\right)^{-6/5} \qquad (8)$$

$$d(t) = \left(\frac{\pi}{6}\right)^{-1/3} \left(k_t f_v t\right)^{2/5} \qquad (9)$$

The evolution of particles following these approximate equations has been demonstrated in small-scale studies of aerosols formed from combustion systems for fly ash from coal[22,54,55] and soot particles[30,56,57] and waste combustors.[58,59]

As shown by eqs 8 and 9, the number and size of particles can be determined for $n_0kt >> 1$ if the amount of material in the form of the aerosol is known. When f_v is measured from the total amount of submicron ash collected, good agreement is observed between theory and experiment, both for the particle size distribution of the submicron ash[55] and the dependence of the mean particle diameter on f_v.[22]

The value of f_v for the mineral matter is determined by the vaporization kinetics, and is a function of temperature and environment to which the minerals are exposed. The mass of the submicron aerosol is usually dominated by the refractory and alkali metal oxides.[54,60,61] At typical combustion temperatures, the burning rate of a particle is limited by gas-phase diffusion, and the particle is surrounded by a CO-rich reducing atmosphere. The vaporization of the refractory metal oxides is augmented by the reduction of the oxides by CO to form suboxides such as SiO and Al_2O and elemental metals such as Fe, Ca, and Mg. The suboxides and metals will diffuse through the particle boundary layer into the bulk gas where they are oxidized and condense to produce the submicron aerosols. The vaporization rate is strongly temperature-dependent[55,62–64] so that the amount of submicron aerosol will vary with combustion conditions. The vaporization of elements is complicated by their interaction with the minerals in the coal. Sodium, for example, will have its vaporization suppressed either because it may be originally present in sodium aluminosilicates or because it is captured by the alumina silicates after release.[65–67]

Particle Growth by Condensation and Surface Reaction

Vaporized elements distribute on the surfaces of existing submicron and residual ash particles by condensation and chemical reaction. The rate of mass addition to a spherical particle for mass-transfer limited deposition over the entire range of particle size is given by the Fuchs-Sutugin interpolation equation:[6,41]

$$\frac{dm}{dt} = 2\pi c_\infty D d_p \frac{1+Kn}{1+1.71Kn+1.33Kn^2} MW \qquad (10)$$

where c_∞ is the concentration of the condensing species, MW its molecular weight, D its diffusivity, and Kn the Knudsen number, defined as the ratio of the mean free path in the gas to the particle diameter d_p.

For the case in which the rate of deposition is controlled by chemical reaction, the mass flux to the surface is independent of mass transfer and is given by

$$\frac{dm}{dt} = \pi d^2 MW k_s C \qquad (11)$$

where MW is the molecular weight of the depositing species, C is the concentration in the gas, and k_s is the rate of surface reaction. The literature also covers the cases of combined mass transfer and surface kinetics and the additional complication of pore diffusion in porous surfaces.[33,68,69]

Because of the higher surface area per unit mass, smaller particles tend to be enriched in the compounds that condense or deposit on the surface. The trace elements in coal and waste tend to deposit without significantly changing the particle size distribution. For this case, the mass concentration of the depositing species can be readily calculated by integrating the mass deposition of the depositing species along an ash particle trajectory and dividing the mass deposited by the mass of the ash particle, that is,

$$Mass\ Conc(D) = \left. \int_0^t \frac{dm}{dt}\,dt \middle/ \frac{\pi d_p^{\,3}\rho}{6} \right. \qquad (12)$$

Applying eqs 10–12 to the trace elements shows that concentration of trace elements on the surface of the ash can be described as a power function of size, with the concentration increasing as the particle size decreases. The mass concentration dependence upon particle size is therefore proportional to $1/d^n$, where the exponent n for the limiting cases is given in Table 1.

An added case is that of a porous particle with chemical kinetics controlling. For this case, the amount of reaction is proportional to volume, and the concentration of the trace reacting species will be independent of particle size. The dependence will be different for the submicron and supermicron particles since these straddle the gas mean free path in size. The gas mean free path varies from ~0.2 µm at ambient conditions to ~1 µm at combustion conditions, so that ultrafine particles will generally have $Kn >> 1$ and supermicron particles $Kn << 1$. Given that the Kn is the mean free path in the gas (a constant) divided by the particle diameter, eq 10 shows that dm/dt is proportional to d for $Kn << 1$ and to d^2 for $Kn >> 1$.

Table 1. Exponent n in size-dependent mass concentration of trace species: concentration $\propto$ ($1/d^n$)

Controlling Mechanism	Particle Size	Exponent *n*
External Mass Transfer	Ultrafine ($Kn >> 1$)	1
External Mass Transfer	Supermicron ($Kn << 1$)	2
External Surface Kinetics	All Sizes	1
Internal Surface Kinetics	All Sizes	0

The early studies on the size-dependent concentration of elements in fly ash[70–72] all were performed for supermicron particles and showed the $1/d^2$ size dependence expected for mass transfer-controlled condensation. Some studies[21,73] have shown the difference in the dependence on particle size of the trace volatile element concentration between the submicron and supermicron fractions. Other studies have shown an enrichment of the smaller particle sizes in the trace volatile elements.[21,54,60,61,66,69–72,74–84]

The reasons for attention to the size dependence of trace element concentration are that (1) this provides a diagnostic for the mechanism of surface deposition; (2) the enrichment of submicron particles in certain elements affects the total capture efficiency of that element in the APCDs; and (3) elemental concentrations affect the chemical speciation, which can be important for health effects.

The exponent n that best fits the variation of elemental concentration with size can be used to determine the mechanism of deposition, for example, whether it is condensation or surface reaction. Haynes et al.[69] deduced from the size dependence of particle composition that the deposition of As and Sb was controlled by chemical reaction. More extensive studies of the size dependence of the deposition have been carried out[85–87] showing that As, Se, and Sb react with the fly ash to an extent that depends on ash composition, thus leading to a coal-dependent partitioning of the elements between the submicron and supermicron ash.

Elements that deposit by surface reaction or surface condensation are expected to be enriched in the surface layers. Studies using surface spectroscopic techniques have shown that the surface layers of both the supermicron[88] and submicron[21] ash particles are enriched in the trace elements. By ion milling of the particles, one can show the stratification that results from the sequential deposition of elements. The implications of this surface stratification to particle toxicology will be discussed later in this review.

To model the partitioning of trace elements in combustion, one needs the particle size distribution of the submicron and supermicron ash and the amount of each of the trace elements vaporized. Models of the vaporization of trace elements based on equilibrium assumptions[89–91] have been developed for the vaporization and subsequent condensation or chemical surface reaction of trace elements.

The models are based on the assumption of equilibrium between the trace species and the vapor and the residual ash in the combustor. Subsequent condensation and reaction of the trace species is also taken into account. In the model by Sandelin and Backman, two reactors in series are considered to represent the radiant section of a boiler and the ESP, respectively.[90] The partitioning of trace elements in the radiant chamber is calculated for a given fuel composition and fuel/air ratio from equilibrium for an assumed distribution of bottom and fly ash and the temperature of the radiant chamber. The distribution of the elements from the ESP is obtained from the temperature in the precipitator and the ash collection efficiency.

Simulations carried out for a boiler for As, Cd, Hg, Ni, Pb, Se, V, and Zn were found to be in reasonable agreement with experimental observations on an operating power plant. In the paper by Yousif et al., the metal partitioning was calculated by a post processor using input obtained from a computational fluid dynamic simulation of a boiler.[91] The major mass of the ash is distributed between the residual fly ash and submicron ash as inlet conditions. The trace species are assumed to be released at a rate proportional to the char burning rate. The concentration distribution of the trace species is then calculated, allowing for condensation on surfaces and nucleation. The vapor species were assumed to be in equilibrium. Simulations were carried out for Pb and Cd, and their distribution between the residual and submicron ash was found to be in good agreement with experiments on a pilot scale combustor fired with coal and sewage sludge. Nucleation was not found to occur, as the supersaturation did not reach the critical level.

Most studies of trace metals from coal combustion (including some by the co-authors) have reported elemental concentration or enrichment factors since this is what is directly measured by the chemical analysis. Enrichment factor is defined as the concentration of an element in a particular size fraction (e.g., the submicron ash) divided by the average concentration for that element in the total ash. The measured concentration is controlled by the mass balance, and an element may be reported as being depleted in the submicrometer ash solely because of dilution by another element. For example, alkali metals dominate the submicrometer ash from low rank coal, while carbon dominates the particulate emissions from oil and biomass combustion. The raw concentration of transition metals in the total ash from oil combustion is largely an artifact of the combustion efficiency, not a result of the metal vaporization. The relative amounts of elements may be relevant for some health-related studies since the mineral form and valance state of the trace element is often sufficiently described by the equilibrium composition in the bulk ash matrix. For other types of health studies, the absolute amount emitted is of concern. While elemental concentration data is useful, including sufficient data in a publication to calculate a mass balance greatly enhances the value of the particle composition data for reuse in both aerosol formation mechanism and toxicology studies.

Particle Morphology

Soot and submicron ash particles often consist of aggregates of 10–30 nm primary particles. It is important to understand what determines the structure of these particles, since the aggregate size determines the aerodynamic behavior of the particles while the primary particle size determines the surface area.

The coagulation theory described above assumes that particles coalesce on collision. This assumption is valid as long as the coalescence time is short compared with the time between particle collisions. For inorganic particles, coalescence times can be calculated assuming surface tension-driven viscous flow using the theory of Frenkel

$$t_c = \frac{\eta r}{\gamma} \qquad (13)$$

where η is the viscosity, and γ the surface tension. Alternatively, the coalescence time can be determined by solid-state sintering[92,93]

$$t_c = \left(\frac{\Delta L}{L_0}\right)^{5/2} \frac{\sqrt{2}kTd_p^{\,3}}{160D^{*}\gamma a^3} \qquad (14)$$

where DL/L_0 is the fractional shrinkage in diameter of two spheres, D^* is the self-diffusion coefficient for the mobile species, and a^3 is the atomic volume of a diffusing vacancy. As long as the characteristic coalescence time is much smaller than the time between collisions, the particles will coalesce and maintain their sphericity. The coalescence time increases because of the increase in particle diameter and the decrease in temperature (leading to an increase in η or a decrease in D^*). After a time, which depends on the combustion conditions, the colliding particles will begin to form aggregates. This transition has been studied for coal combustion aerosols and for the flame synthesis of particles.[19,94–96]

The aggregates that are produced have a fractal dimension, D_f, which provides the scaling parameter relating the number of particles n_a in an aggregate to the ratio of the radius of gyration r_g and the primary particle size r_0:[95]

$$n_a \propto \left(r_g / r_o\right)^{D_f} \qquad (15)$$

where D_f has values of 3 for a solid sphere and of 1 for a string of particles. For soot and submicron ash particles, the value of D_f is about 1.7.[95,97,98] The theory for the coagulation of aerosols has been extended to aggregates, and a two-dimensional solution was obtained allowing for coagulation and sintering.[99,100] Application of this theory shows the aggregates still assume a self-preserving size distribution but with a wider size distribution than that for spherical particles.

For soot particles, there are several hypotheses for the formation of aggregates.[37,39,101] One of these is that the soot precursor particles are liquid polymers[38] and will coalesce after collision. In parallel, the liquid polymers will dehydrogenate and their viscosity will increase, leading to a transition from coalescence to aggregation similar to that described above for inorganic aerosols. A second hypothesis[37] is that the soot particles form as a solid, then collide and aggregate. Surface growth occurs in parallel with growth by collisions. If the surface growth is sufficiently rapid, the particles in the growing aggregate will be immersed in the deposited carbon and the resulting structure will appear as a spherical particle. Numerical simulations support this hypothesis when realistic values of surface growth and coagulation are used.[37] As the particle size increases, and as the species contributing to surface deposition are depleted, the rate of surface growth due to deposition will decrease. After this point, the soot particles will develop as aggregates with a fractal structure.

The final particle morphology at the exit of the high-temperature zone is the result of multiple processes. The characteristic times for these processes can be readily predicted, and examination of particle morphology gives a good indication of which processes are dominant for the given situation. This type of analysis was applied to the behavior of sorbents for toxic metal control.[102]

Residual Ash Formation

Submicrometer particles dominate the number count of particles emitted by combustion sources and very often dominate the surface area as well, but the mass of PM emissions is usually dominated by the organic or inorganic residue of material that remained in a solid or liquid phase throughout combustion. These particles are referred to as residual ash. The residual ash formation process differs from the formation of the submicrometer particles by molecular weight growth processes for soot and by vaporization and condensation for inorganic ash, as described above. The total amount of noncombustible minerals in the residual ash is determined by the mass balance, and the total amount of carbonaceous material in the residual ash is determined by the combustion efficiency.

Most fossil fuels contain inorganic components. For U.S. coals, this inorganic content constitutes ~10% on average of the mass. For petroleum, the maximum ash mass ranges from 0.05% for a light No. 4 oil to 0.15% for a No. 5 fuel oil; a typical value No. 6 or residual oil ash content is 0.8%.[103] A representative ash content for wood is 2.5%, but it varies widely.

Figure 3 illustrates the major processes affecting the formation of submicron and supermicron ash during the combustion of coal, biomass, and oil.[69,73] The mass of particle emissions measured at the combustion chamber exit is determined by a number of complicating factors. The first is that, depending upon the type of combustor, only a fraction of the total ash content in the fuel is carried over with the combustion gases as fly ash. The so-called bottom ash is deposited in the ash hopper on the floor of a suspension-fired furnace or is dropped off the end of the grate in a stoker-fired furnace. The ash entering the particulate control equipment downstream from coal-fired boilers varies from 10% of the total fuel ash content for cyclone or wet-bottom furnaces to 85% for dry-bottom pulverized coal-fired furnaces. The fly ash particle size distribution is multimodal. The factors that control the residual ash size distribution will be discussed below for the case of pulverized coal-fired systems, partly because pulverized coal has been most extensively studied, and partly because these boilers account for a large portion of the primary energy production worldwide.

The noncombustible matter in pulverized coal includes mineral grains of clays, pyrites, and quartz that vary in size from less than a micron to the largest sizes that can pass through the pulverizers, which is over 300 μm. Part of the inorganic matter is included in the coal matrix as discrete crystals, some is incorporated in the organic matrix as organo-metallic complexes or as ion-exchanged metals bound to the organic acids, and some of the minerals are present as extraneous particles. These forms of inorganic matter are shown schematically in Figure 4.[104] Detailed characterizations of the mineral content of coals have been conducted by computer-controlled scanning electron microscopy (CCSEM) by a number of research groups.[105–111] An example of the mineral size distributions as determined by CCSEM is provided in Figure 5, which shows the size distribution of mineral inclusions in raw Kentucky No. 11 coal. The kaolinite and illite inclusions are found in the smaller particle sizes while calcite and pyrites are in the larger particle sizes. Quartz and mixed silicates are distributed over all size ranges.

Given the mineral distribution within the pulverized coal, one can calculate the ash particle size distribution using a material balance. Assume a coal particle of density ρ_c and diameter d_c, and a mass fraction f_a yields n ash particles of density ρ_a and diameter d_a. A mass balance then yields the

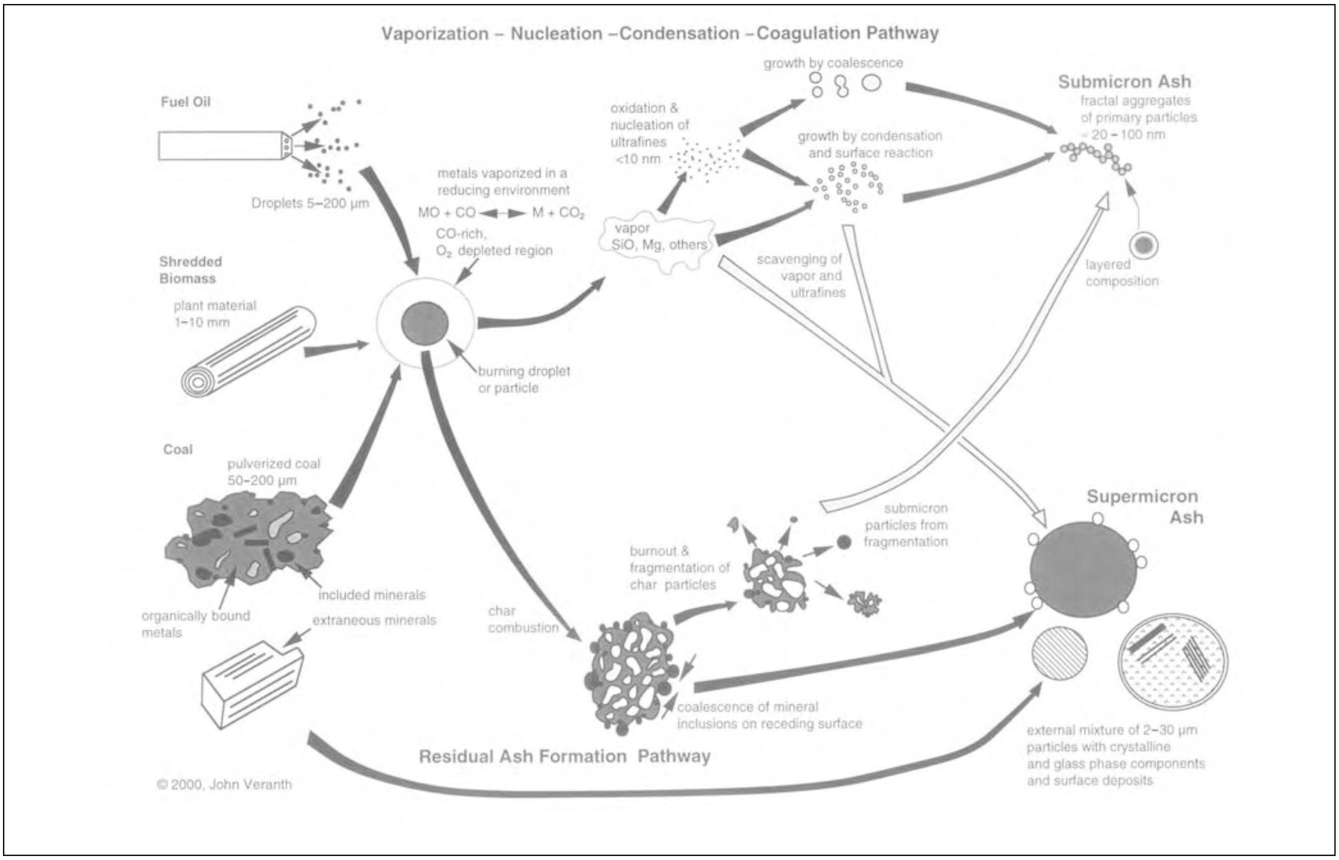
Vaporization – Nucleation – Condensation – Coagulation Pathway
Fuel Oil
Droplets 5–200 µm
Shredded Biomass
plant material 1–10 mm
Coal
pulverized coal 50–200 µm
organically bound metals
included minerals
extraneous minerals
metals vaporized in a reducing environment
MO + CO ⟷ M + CO₂
CO-rich, O₂ depleted region
burning droplet or particle
vapor SiO, Mg, others
oxidation & nucleation of ultrafines <10 nm
growth by coalescence
growth by condensation and surface reaction
scavenging of vapor and ultrafines
Submicron Ash
fractal aggregates of primary particles ≈ 20 – 100 nm
layered composition
char combustion
burnout & fragmentation of char particles
submicron particles from fragmentation
coalescence of mineral inclusions on receding surface
Supermicron Ash
external mixture of 2–30 µm particles with crystalline and glass phase components and surface deposits
Residual Ash Formation Pathway
© 2000, John Veranth

Figure 3. Formation of inorganic submicron and supermicron particles during combustion of solid and liquid fuels. Submicron particles are formed by the vaporization–nucleation–coagulation pathway. Supermicron particles are formed by the residual ash pathway. Based on earlier versions.[69,73]

following expression for the diameter of the ash particle:

$$d_a = d_c\left(\frac{f_a\rho_c}{n\rho_a}\right)^{\frac{1}{3}} \tag{16}$$

To apply this simplified relationship, assume that the coal specific gravity is constant and equal to 1.3, that the ash specific gravity is constant and has a value typical of glass of ~2.5, and that each coal particle yields one ash particle, that is, that $n = 1$. For these assumptions, a typical U.S. coal with 10% ash ($f_a = 0.1$) yields a ratio of the ash particle diameter to the coal particle diameter, d_a/d_c, of 0.37. A pulverized coal with a mean coal particle diameter of 50 µm would yield a mean ash diameter of ~19 µm

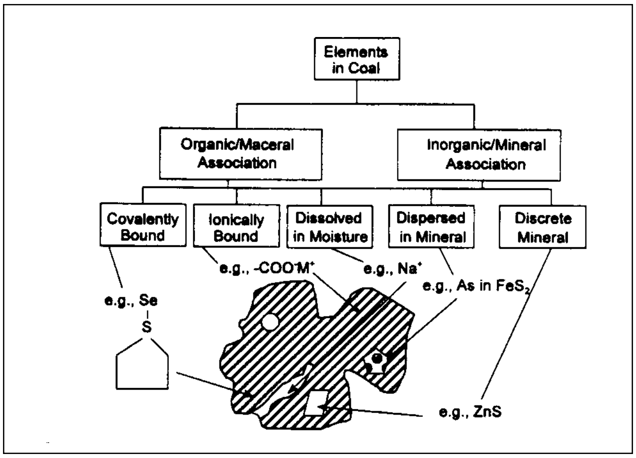
Elements in Coal
Organic/Maceral Association
Inorganic/Mineral Association
Covalently Bound
Ionically Bound
Dissolved in Moisture
Dispersed in Mineral
Discrete Mineral
e.g., Se
S
e.g., -COO⁻M⁺
e.g., Na⁺
e.g., As in FeS₂
e.g., ZnS

Figure 4. Classification scheme for describing the modes of elemental occurence in coal. Reproduced by permission of Elsevier Science.[104]

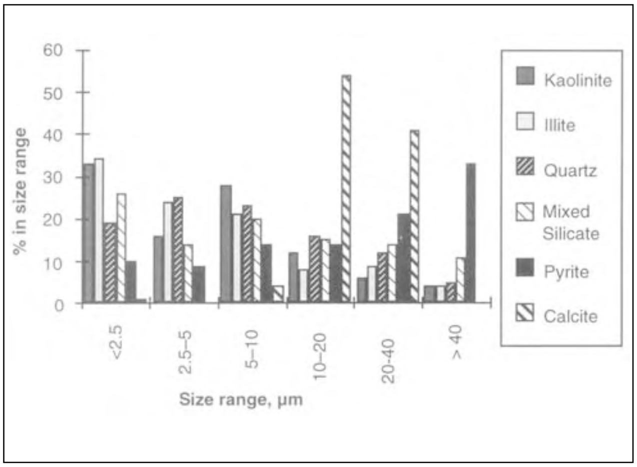

Figure 5. Size distribution of minerals in Kentucky coal. Quartz, kaolinite, and illite are concentrated in the smaller size fractions, while pyrite and calcite are concentrated in the larger sizes. Based on data in ref 111.

under these assumptions. This is a reasonable default value, but the actual transformation mechanisms are more complicated. One needs to account for the different ash content of each coal particle, which will result in variations in both f_a and r_c. The fragmentation of coal char during combustion and the incomplete coalescence of mineral droplets on the shrinking surface both yield values of n other than unity. Also, the ash particle density ρ_a varies due to changes in composition of individual ash particles and to the presence of gas bubbles within the ash.[112–114]

The mineral inclusions are not distributed evenly between different coal particles. Some particles are nearly inclusion-free and some of the particles are pure minerals (the extraneous ash). The actual distribution of the minerals between the different coal particles is provided by CCSEM.[109,115] If such information is not available, an approximate distribution can be obtained by assuming that the minerals are randomly distributed between coal particles.[116–119] The ash particles will have a particle-to-particle variation in composition that will reflect the variation in the mineral content of the individual coal particles from which they are produced. This is illustrated in Figures 6 and 7, which show the Al, Si, and Fe distributions both in the parent coal minerals and in the resulting fly ash, respectively.

The number of ash particles, n, produced by a coal particle will depend upon the competition between coalescence of molten mineral inclusions and fragmentation of the char particle during combustion. The ash produced by the mineral inclusions in coal will adhere to the char surface as it burns and will coalesce with other ash particles as the char surface recedes.[120] The fragmentation of chars has been shown to depend upon the macroporosity of the chars[114] and therefore upon the swelling behavior of coals, dependent upon coal-specific pyrolysis behavior. While complex models have been developed to predict fragmentation behavior,[113,121–124] validation of these models has been limited, and complicating factors such as adhesive forces have been neglected in past analyses.[125] The models provide useful qualitative information but cannot predict quantitative trends with confidence. The fragmentation scales with the ratio of the volume fraction of ash in the char to the void fraction, Λ.[122] For high values of Λ, fragmentation is negligible, and one ash particle is produced per coal particle. For low values of Λ, extensive fragmentation occurs, and each mineral inclusion produces a separate ash particle. These trends are well illustrated by the results of Wu et al., who showed that as pressure increases during pulverized coal combustion, the macroporosity increases and the ash produced becomes finer.[126]

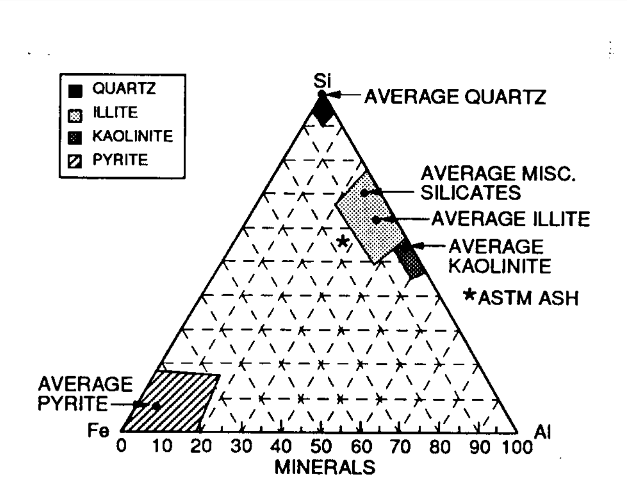

Figure 6. Si-Al-Fe ternary diagram showing typical composition ranges from minerals in coal. Reproduced by permission of Engineering Foundation.[111]

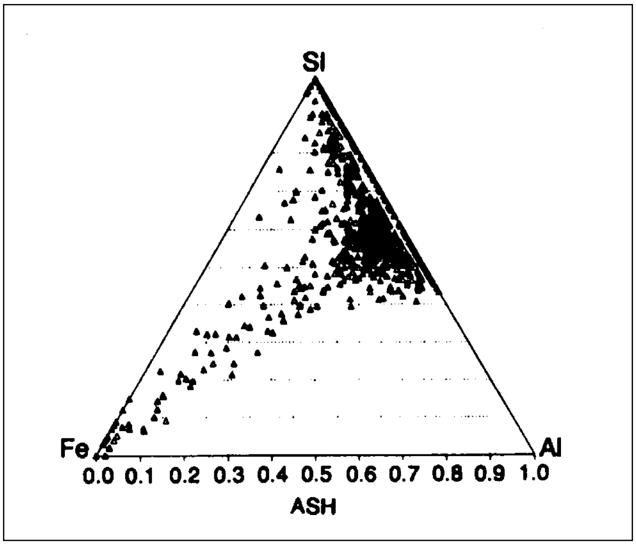

Figure 7. Measured elemental compositions in individual coal fly ash particles. Reproduced by permission of Engineering Foundation.[111]

The particle-to-particle variation in particle density is an added complication. Figure 7 shows that a typical ash sample is a mixture of particle compositions. A number of the ash particles have high iron content and may be expected to have densities more than twice that of the aluminosilicate-rich particles. In addition, a large number of the particles will form cenospheres (hollow spheres) or plerospheres (hollow sphere surrounding a number of spherical ash particles).[83,112,127,128] The mechanism for the cenosphere is the formation of gas within the ash particle in a temperature window where the viscosity is low enough to favor the bubble growth but not so low as to have the gas escape and the bubble collapse. One mechanism for cenosphere formation identified by Raask[128] is the reaction within the ash of iron oxide with carbon to form CO. The cenospheres can grow to sizes up to 300 μm. Up to 5% of the fly ash has been observed to form cenospheres having a specific gravity less than 1.0.[112,128] If a 50-μm particle with a specific gravity of 2.5 formed a cenosphere with an outer diameter of 100 µm, the wall thickness would be ~2 µm and the specific gravity of the particle would be 0.625. The wall thickness decreases with the square of the diameter of the cenosphere and therefore will be submicrometer for the largest cenospheres (>300-µm diameter). Indeed, it has been postulated[83] that one source of the submicrometer particles is provided by the fragments of cenosphere shells.

It can be seen that the multimodal distribution of combustion particles is governed by a number of factors. The submicrometer fraction is generated by the vaporization and condensation of particles and, to a lesser extent, the fragmentation of cenospheres. The supermicrometer particle size distribution is governed by the size distribution of the coal, the mineral matter distribution within each size fraction, the fragmentation of the char during combustion, and the formation of cenospheres. Although the processes governing the size distribution of fly ash are well understood qualitatively, they are sometimes difficult to quantify, most particularly the char fragmentation during combustion. The simple models of one ash particle per mineral inclusion and one ash particle per coal particle provide limiting solutions for the impact of fragmentation. A comparison of experimental data with these limiting solutions is shown in Figure 8 for one case. Because of the importance of fly ash as an additive for concrete manufacture, there are extensive compilations of fly ash size distribution and composition.[129,130]

Special Considerations for Large and Small Particles

Combustion particle diameters range from nanometers to millimeters, a size range which represents a mass range of a factor of 10^{18}. Special considerations are needed for both size extremes. The behavior of the largest particles is dominated by gravity settling, and they are usually considered as bottom ash rather than as aerosols, but this is an arbitrary distinction from a particle formation standpoint. Most reported measurements of combustion particles from coal, biomass, and even from oil are truncated at the upper end by the cutoff of the sampling apparatus. While these macroscopic particles are of no concern for inhalation toxicology, they are important for closing mass balances in both laboratory and full-scale measurements.

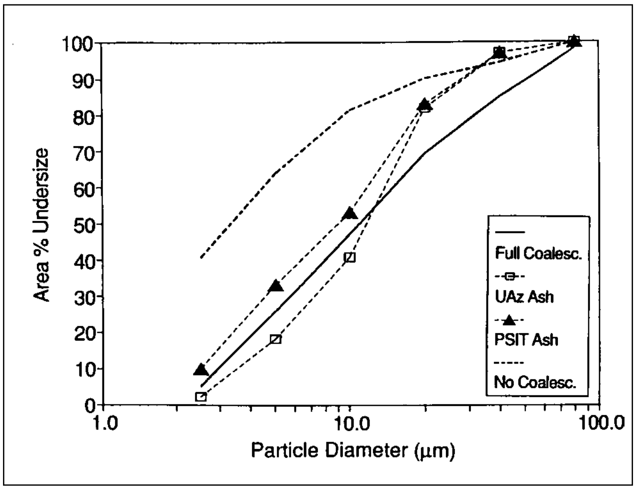

Figure 8. Ash particle size distributions (PSDs), model (solid and heavy dashed line) vs. experiment (symbols) for Upper Freeport coal. Reproduced by permission of Engineering Foundation.[111]

The fume formed by nucleation and condensation of vaporized ash, ash, and organic materials is typically a combination of true nuclei, a transient mode of nuclei that have undergone coagulation and surface growth, and accumulation-mode particles, depending on the relationship between the characteristic time for coagulation and the age of the aerosol when it arrives at the sizing instrument. Combustion particle number size distributions often show a truncated curve with the number of particles in each size range still increasing as the small size limit of the instrument is reached. This suggests a pool of particles exists below the 5–10 nm cutoff[131] of most current particle-size instruments.

Recently, the existence of high concentrations of 1–2 nm combustion particles has been reported.[132,133] These particles cannot be detected by most instruments used for studying submicron aerosols, but can be detected by light scattering and absorption in the near UV. They have a longer life span than would be expected from the coagulation rates discussed above. In the conventional coagulation models, the assumption is made that the sticking coefficient is unity; that is, every collision results in coalescence or aggregation. This is a reasonable assumption for accumulation mode particles; however, nuclei particles on the order of 1–2 nm may have lower sticking coefficients, as was shown by Narsimhan and Ruckenstein in a theoretical study of equal-sized neutral particles that considered the competing effects of van der Waals attraction and Born repulsion.[134]

Acid Aerosols

H_2SO_4 may be considered as either a gas-phase or particle emission depending on the sampling method. Some portion of the total sulfur in the fuel is converted to SO_3 and forms H_2SO_4 in the presence of water in the hot combustion products. The dew point of H_2SO_4 in the undiluted combustion products from fossil fuels is much higher than ambient temperature, and the acid may nucleate and condense to form aerosol particles as the gas is diluted and cooled, either in the unconfined stack plume or in a dilution sampler. Filter-based particle mass measurement methods in which the undiluted gas is passed through a heated sample train can result in the acid remaining in the gas phase. On-line particle number measurements typically require diluting the stack gas to bring the concentration within the range of the instrument, and this results in the acid being measured as PM.

The amount of acid aerosol formed depends on the partitioning of sulfur between SO_2 and SO_3 and on the temperature and humidity of the dilutant gas. The formation of SO_3 is kinetically limited and can be enhanced by catalytic reactions with metals in coal combustion ash[135] or in catalytic NO_x reduction equipment. Typical acid dew points for coal combustion are 380–395 K.[136] For aircraft engines at cruise altitude, the SO_3 measurements are much higher than expected based on hydroxyl and atomic oxygen reaction rates, suggesting another, possibly heterogeneous, pathway.[137] The influence of dilution conditions on aerosol formation are discussed in the measurements section.

Particle Shrinkage by Evaporation and Oxidation

Unlike inorganic oxide particles, which are stable under post-combustion conditions, both condensable aerosol and soot mass can decrease after particles are formed. The organic aerosol, H_2SO_4 aerosol, and hydrated species can evaporate at rates that are well described by local phase equilibrium and diffusion mass transfer rate equations. Soot is destroyed in the flame by oxidation, and soot emissions are much lower than the initial soot volume fraction that occurs in the fuel-rich zones. The rate of soot oxidation can be estimated from the semiempirical kinetic formula proposed by Nagle and Strickland-Constable.[138] However, this correlation overstates soot oxidation at temperatures below 1800 K[34] and understates the oxidation rate in low-oxygen conditions where OH radicals are important.[33] The fractal aggregate structure typical of soot particles further complicates soot oxidation estimates because simple spherically symmetric mass diffusion equations are a poor approximation.

CONTROL DEVICES

The particles emitted from the stack will have a size and composition distribution very different from that in the combustion system because of the size-dependent collection efficiency of any APCD equipment. Historically, the combustion and atmospheric emission research communities have been uncoupled. Combustion researchers generally concentrate on the particulate formation in the flame zone of laboratory and pilot-scale equipment, since this allows close control of experimental conditions. Most field emission studies focus on measurements in the stack, since stack PM is of regulatory concern. Measurements of uncontrolled emissions at the exit of an industrial-scale combustion chamber are difficult and expensive, so data are seldom collected. The particle emission mass measured downstream of modern, high-efficiency particle-removal equipment largely reflects variations in gas-cleaning efficiency, not changes in combustion conditions. However, some details of the primary combustion particles, such as particle morphology and elemental concentration within an aerodynamic size range, are preserved from the combustion chamber to the stack. A few researchers have studied the particles upstream and downstream of the APCD. For example, Itkonen and Jantunen present graphs of elemental size distribution upstream and downstream of the ESP from a plant that co-fired peat and oil.[139] These studies provide an important link between particle formation in combustion and human health impacts.

Gas-cleaning equipment for particle removal includes cyclones, fabric filters, ESPs, and scrubbers on stationary furnaces. Internal combustion engines are equipped with catalytic converters, and particle traps are coming into commercial use on diesels. Particle removal requires some combination of inertial separation, which becomes more efficient with increasing particle size, and diffusion to a solid or liquid collection surface, which becomes more efficient with decreasing particle size. The result is that the removal efficiency of particles from air is least efficient in an intermediate size range from 0.1 to 1 μm. This minimum PM removal efficiency is observed in post-combustion cleanup equipment at the source, in the atmosphere, and in the respiratory system. The fundamental physics of these particle removal processes are covered in aerosol texts,[51] and the related equipment design and performance equations are covered in air pollution control handbooks.[140–142] The stack emissions of specific combustion particle types depends on both concentration of particles in each size range at the combustion chamber exit and on the size-dependent collection efficiency in the gas-cleaning equipment. Understanding the particle size and composition at the source allows developing computational models that can predict practical information such as the penetration of each trace element through an ESP installed on a coal-fired power plant.[143]

The collection efficiencies of three types of particle collectors are shown in Figure 9.[144] The minimum efficiency for all three devices is in the range between the regimes of deposition by inertial and diffusional processes. For a given technology, the actual efficiencies will, of course, vary widely with changes in design and operational parameters. A measure of the wide variation in the penetration of particles through operating ESPs at power plants is provided by Helble[143] and summarized in Figure 10. Again, the peak penetration occurs in the 0.1- to 1-μm size range, where the particle size is comparable to the mean free path of the gas. The collection efficiency of the

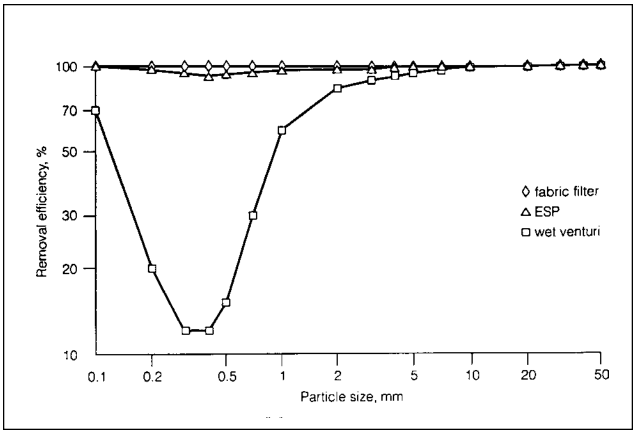

Figure 9. Removal efficiency of three common particle removal technologies used on large stationary combustion systems. Reproduced by permission of IEA.[144]

smallest particles by an ESP is reduced because a portion of the incoming ultrafine particles do not receive a charge (partial charging).[145–147] However, in the ultrafine size range, diffusion and particle growth by condensation of water vapor become important removal mechanisms.

Since the collection efficiency of a particle control device is size-dependent, the varying partitioning of elements between the submicron particles, residual fly ash, and vapor will lead to a wide range of elemental collection efficiencies that will differ from the overall PM collection. Kauppinen and Pakkanen reported the emissions of 17 elements by particle size based on measurements in the stack of a coal-fired power plant equipped with an ESP.[148] Three elements are shown in Figure 11. Aluminum is found in the supermicron particles, while sulfur is found in particles smaller than 0.1 μm. Cadmium shows a bimodal distribution.

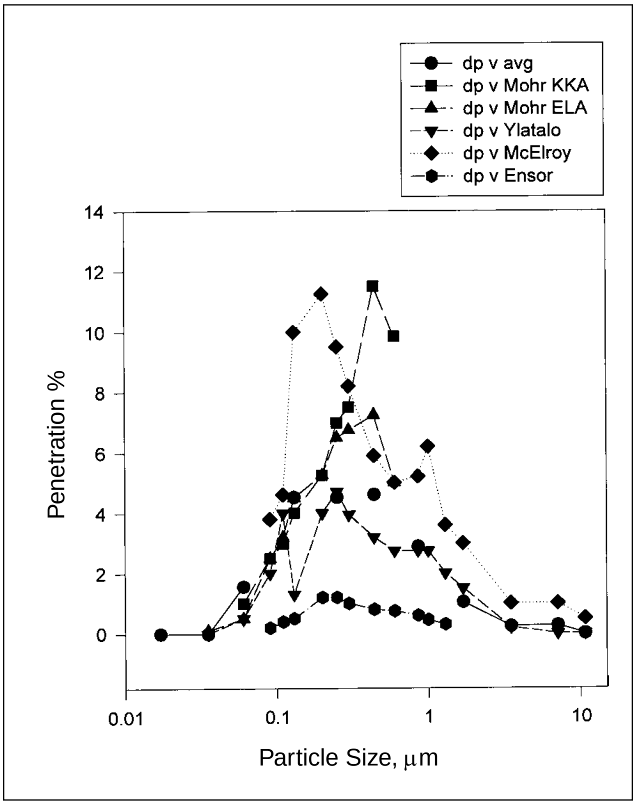

Figure 10. Summary of studies reporting penetration of coal fly ash through an ESP. Reproduced by permission of Elsevier Science.[143]

Extensive data have been obtained by EPRI and the U.S. Department of Energy (DOE) on the collection efficiencies of coal-fired utility boilers for the elements regulated under the Air Toxics provision of the Clean Air Act

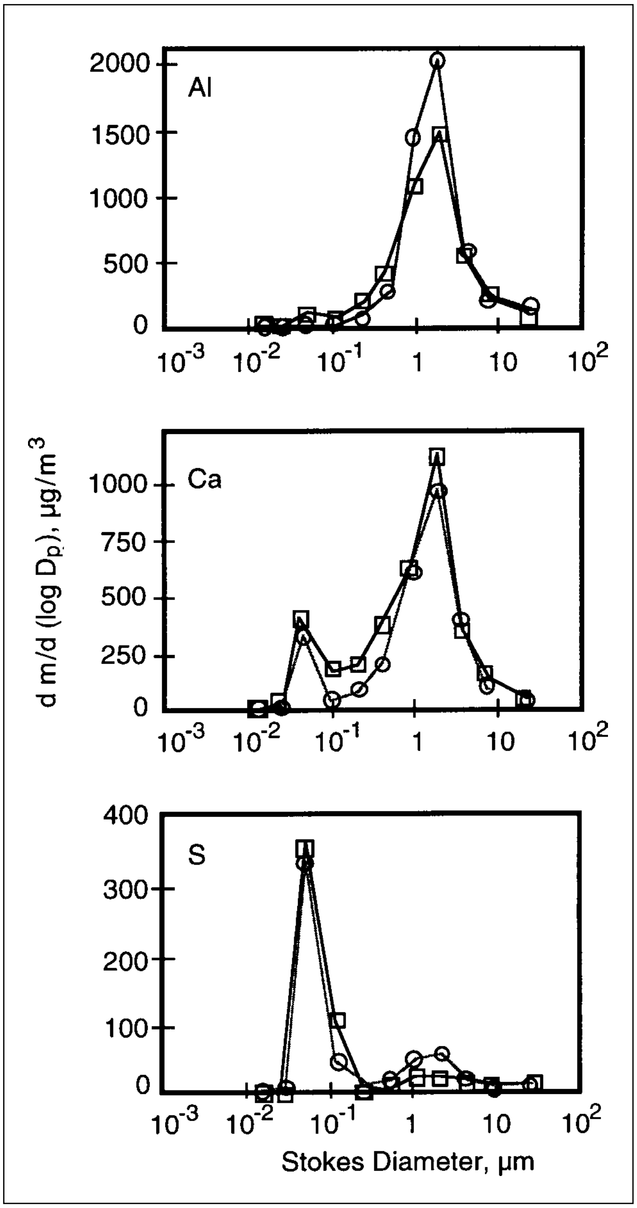

Figure 11. Distribution of selected elements by particle size as measured in the stack of a power plant equipped with an ESP. Some elements, such as Al, are concentrated in the large particles, while others, such as S, are concentrated in the submicron particles. Some elements show a bimodal size distribution. Replotted from more complete data presented by Kauppinen and Pakkanen.[148]

Amendments.[149–151] These data will be used to illustrate the relationship between combustion emissions and stack emissions. The data on the collection efficiencies of particles and elements in ESPs compiled by Helble[143] is summarized in Table 2. The collection efficiency for some elements approaches the overall particle collection efficiency. Elements enriched in the fine particles have a slightly lower collection efficiency. Metals with high vapor pressure, Hg and Se, have a much lower collection efficiency across the ESP than the total particle removal. A wet scrubber for SO_2 removal also selectively removes species adsorbed on particles and can cause chemical reactions on the particles by humidification at moderate temperature and entrainment of chemicals from the sorbent solution.[152] Additional aqueous-phase and photochemical reactions can take place in the stack plume and atmosphere.

Correlations between the emissions of elements from a boiler with the mass of elements fed with the coal[150] do not provide any insights on the effect of combustion conditions on the emissions. It is desirable to develop models to determine how the emissions are influenced by changes in combustion operating and design parameters. Laboratory studies have provided the mechanism for vaporization and condensation processes that govern the size and composition of the ash that can be used to develop ash transformation models. To be able to determine the effect of changing combustion modifications or changing APCD performance, one needs to combine a size-dependent model of emissions with a size-dependent model of APCD performance. Such a model has been developed by Helble in his retrospective analysis of the EPRI and DOE field studies of air toxics emissions.[143] For the fundamental combustion particle studies to be useful to the regulatory and health communities, more attention needs to be paid to the role of the downstream heat transfer sections, the APCD, and the initial plume condensation in modifying composition and size distribution of the emissions from the combustor. Until suitable integrated computational models of the downstream processes are available, the best measures of the contribution to human exposure from various combustion sources will be empirical data from stack or exhaust measurements.

Table 2. Field data on trace element capture efficiencies in ESP.

Element	ESP Capture Efficiency	Metal Capture/ Particle Capture
Vapor-Phase Metals		
Hg	28.9%	0.29
Se	49.1%	0.49
Fine-Particle Enriched		
As	96.1%	0.969
Pb	96.8%	0.976
Not Enriched in Fine PM		
Co	98.2%	0.992
Mn	98.5%	0.993

Note: Elemental capture in the ESP depends on the size-dependent partitioning of the metal to particles. Data from Helble.[143]

A summary of the emissions from these four different combustion applications follows. It should be noted that there is wide variability in both the source PM and in the downstream particle removal efficiency depending on fuel type and combustor size. Coal-fired boilers are equipped with high-efficiency APCD and emit particles enriched in the 0.1–1 μm range, where the particle removal efficiency is at a minimum. Oil-fired boilers often do not have any APCD because of the low ash and sulfur content of the fuel. As a consequence, large particles, such as coked fuel residue, may be emitted in addition to the submicron condensation aerosols. Small combustors, such as fireplaces and open burning, do not have any particle control devices.

SPECIFIC COMBUSTION APPLICATIONS

This section discusses the particle emissions entering the atmosphere from various practical combustion applications, both with and without post-combustion particle removal and gas cleaning. Typical data on PM mass emissions, size distribution, and composition are provided for convenient reference. The citations can serve as a starting point for a literature search, but a comprehensive review of the literature for each of these individual applications is not attempted. The extensive compilation of combustion emission factors prepared by the EPA[153] emphasizes PM_{10} mass and provides little data on particle number distribution or on chemical composition of the PM.

Residential and Commercial Boilers and Furnaces

Distillate fuels, generally kerosene and No. 2 fuel oil, are widely used for domestic and process heat in areas where natural gas is unavailable. Direct population exposure to oil combustion emissions occurs because the fuel is burned in populated areas, and the furnaces do not have post-combustion particulate controls. The PM is mainly sulfate aerosol from fuel sulfur and soot plus organic aerosol from incomplete combustion. The ash content of distillate fuel is small, but not zero, so the emissions also contain inorganic components. In a study of homes with and without kerosene space heaters, the kerosene heaters were estimated to add ~40 μg/m^3 of total $PM_{2.5}$ and 15 μg/m^3 of SO_4^{2-} to the indoor air.[154] Hildemann reported that the emission factor for particles smaller than 0.7 μm from an industrial-scale boiler fired with No. 2 fuel oil was 8 μg/kJ of fuel.[155] These boiler emissions contained a mode near 50 nm and a larger mode near 0.5 μm. The fine particles consisted of about 32% sulfates, 29% EC, 6% organics, 6% NH_4^+, and 3% other ionic and oxidized trace species (mainly SiO_2, Al_2O_3, Fe_2O_3 and Na^+).[156] The balance of the mass was in unidentified substances and may have included water in the form of hydrolyzed compounds. Detailed composition of the organic carbon (OC) portion of oil-boiler PM was also reported.[157]

Residual Oil Fly Ash

Residual fuel oil is a highly viscous product that has a much higher ash content than distillate fuels, since the metals in the crude oil, as well as contamination from refinery catalysts and equipment, are concentrated in this fraction. Residual fuel oil is burned in some power plants, for example, in the eastern United States. Similar heavy fuel oil grades, Bunker C and marine diesel, are burned on ships, and these emissions are suspected to have a significant air quality impact on coastal cities. Metal mobilization from residual oil fly ash has been extensively studied[158–160] because of the high content of V and Ni, which is different than other combustion PM.

The emissions from residual oil are multimodal, with a mode centered at 70–80 nm, but with most of the mass in a residual ash mode composed of cenospheric carbon-rich particles extending beyond 100 μm in diameter. Carbonaceous material can be greater than 75% of the mass emissions from small residual oil-fired boilers.[161] The formation of carbonaceous PM during residual oil combustion is related to the asphaltene content of the fuel.[162,163] When the residual oil is burned more efficiently under conditions typical of a utility boiler, the carbon content is lower and the PM is almost entirely in the ultrafine (condensation) mode.[164] The transition metals in residual oil combustion ash are in the form of sulfates rather than sulfides or oxides.[165–167]

Coal-Fired Steam Generation Boilers

The stack emissions from coal-fired utility boilers are affected by the particle generation during combustion and by particle transformations and size-selective removal during cool-down and gas cleaning. Power plant coal combustion including pollutant formation,[168,169] ash formation and deposition,[115] submicron particle formation,[14,66,170] and metal transformation[73] have been reviewed. The inorganic particle stack emissions consist of a supermicron mode containing spheres of mineral ash and a submicron mode formed by mineral vaporization and condensation, as discussed above. The carbonaceous emissions consist of supermicron char particles remaining from incomplete combustion of the parent coal. Submicron carbon-rich particles, suggestive of soot, are also present in the exhaust from both laboratory- and full-scale coal combustors.[171–174] Figure 12 shows the cumulative mass emissions versus size for a sample of power plants including both pulverized coal and cyclone burners.[118,175,176] The multimodal size distribution of the emitted PM is indicated by the changes in slope of the cumulative mass curve. Full-scale data show that an ultrafine particle mode can be detected for both circulating and bubbling fluidized bed coal combustion, but the ultrafine concentration is several orders of magnitude smaller than the ultrafine PM concentration produced by pulverized coal combustion.[177,178]

Many of the field studies of coal-fired power plants were aimed at obtaining the information needed for regulatory purposes, so the measurements have focused on the total mass of the emissions. Selected field studies have determined the fractions of the trace elements entering a boiler that enter the flue gases and pass out of the unit through the stack.[63,78,88,148,152,179,180] Additional efforts have focused on the effectiveness of APCDs in removing these potentially toxic substances.[63,78,179,180] These studies provide the following information:

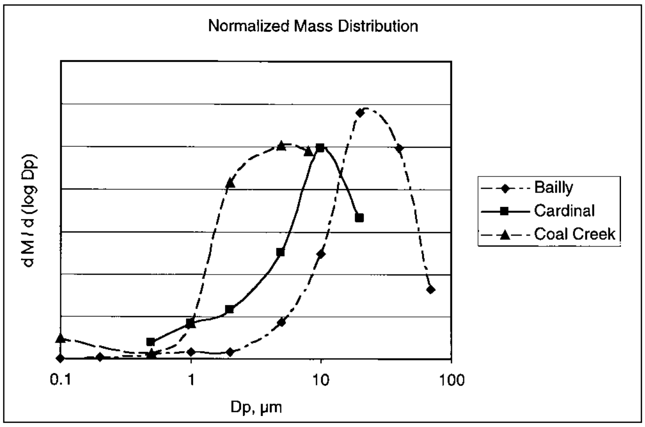

Figure 12. Normalized differential particle mass distributions measured in the stack for a sample of coal-fired power plants using different burner and gas-cleaning technologies. Data compiled from DOE field studies in 1993–1994.[118,175,176] The stack particle mass emission rates vary between replicate runs by about a factor of 2 due to sensitivity to plant operating conditions.

Plant	Description	Stack Emissions
Bailly	345 MW, Cyclone Burner Dry scrubber, ESP Illinois high-sulfur bituminous	60 kg/hr
Cardinal	615 MW, well-mounted cell burner ESP, no sulfur removal Pittsburgh No. 8 bituminous	100 kg/hr
Coal Creek	550 MW, tangential-fired Wet scrubber, ESP North Dakota lignite	260 kg/hr

- The inorganic ash size distribution is multimodal. The submicrometer particles consist of aggregates of primary particles that have grown to 10–50 nm. The larger particles consist of spherical particles, including cenospheres and plerospheres.[120,127,181]
- Particles entering the APCD are essentially bimodal in terms of mass, with on the order of 1% of the ash consisting of submicrometer particles and the larger residual ash falling into the 1–20 μm range.[54,63,180,182]
- Particles in the 0.1–0.3 μm range have the highest penetration through APCD compared with both larger and smaller particles,[63,78,179,180] so the 0.1–1 μm particles form a larger fraction of the mass distribution leaving the APCD than they do in the uncontrolled combustion emissions.[63]
- The submicrometer ash is enriched in volatile elements relative to the larger particles.[148,152] The concentration of the trace elements within the submicrometer and supramicrometer ash fraction increases with decreasing particle size.[73,88]
- The surfaces of the ash particles are also enriched in volatile elements relative to their core.[88]
- The major influence on the fraction of ash that is vaporized is the temperature.

Because NO_x is also temperature-dependent, a correlation between high NO_x emissions and high amounts of submicron particles has been reported[55,64,76] for boilers in which the thermal (Zeldovich) kinetics dominate the NO_x emissions. For modern, post-New Source Performance Standards boilers, the NO_x emission is dominated by fuel nitrogen. The correlation between NO_x and submicron particle formation is not as well established for these conditions, since conversion of fuel nitrogen to NO_x is controlled by staging the air, and NO_x formation does not necessarily correlate with temperature.[183–185]

Metals may partition into three major emission streams: the stack, the bottom ash, and the fly ash collected during gas cleaning. An example of this type of data, summarized in Table 3, shows the points in the power plant process where As, Cr, Hg, and Se are removed and the fraction of that element in the raw coal that is emitted from the stack.[186] The toxic metals in the PM emissions are the result of fuel composition, combustion conditions, and downstream cleanup. Coal washing can greatly reduce the input of toxic metals to the boiler. A small fraction of the volatile metals is removed with the bottom ash, some metals are adsorbed on particles and removed in the ESP, and flue gas desulfurization systems can remove metal ultrafines and vapors. Metal emissions from coal-fired steam generation boilers are not currently regulated in the United States. Table 4 lists typical physical characteristics and chemical composition of coal fly ash.[129,130,187–189] Coal fly ash typically contains less than 5% unburned carbon, but problems with char burnout can result in much higher carbon values.[125,190–192]

Table 3. Elemental partitioning in a coal-fired power plant.

	Coal Washing	Boiler Bottom Ash	ESP or Fabric Filter	Flue Gas Desulfurization	Emitted from Stack
As	65–75	0–2	85–99	0–20	0–5
Cr	30–75	3–20	85–99	0–20	0–2
Hg	30–40	0	0–60	10–90	5–95
Se	25–50	0–5	10–80	0–50	20–80

Note: Data obtained during the DOE PISCES program shows the percent of the element in the raw coal that is removed at various points in the process. Based on original DOE report and other reports.[186]

Elemental balances on power plants show that ~1–4% of most metals in the fuel are emitted in the stack PM.[143,148,152,178,193] The major exceptions are Se and Hg, which escape as vapors. Rapid quenching from high temperature results in the formation of glass-phase species of indeterminate composition rather than the crystalline minerals with similar elemental composition. Optical microscopy on fly ash from ESPs shows that 11–48% of the fly ash has crystallized at the cooling rate normally encountered in boilers. Iron in an alumino-silicate glass is a characteristic phase found in coal fly ash formed under both oxidizing and reducing conditions.[194–196] The presence of large concentrations of alkali and alkali earth elements, typical of western U.S. coals, enhances glass formation and decreases crystallization.[129]

Large-Scale Biomass Combustion

Concerns regarding trade balance, global warming, and disposal of agricultural residue have led to an increased interest in biomass as a renewable energy source. The unique characteristic of biomass PM is the high alkali content, especially K,[197,198] compared to fossil fuel combustion ash. Studies have been conducted of industrial-scale biomass combustion, especially in fluidized bed boilers.[199,200]

The ash formation processes during suspension firing of wood sawdust and sanderdust have been shown to be similar to the mechanism for pulverized coal combustion,[201] as indicated in Figure 3. The supermicron particles are predominantly Ca, but also contain Fe, Al, Mn, and Si. The alkali minerals form a submicron condensation aerosol that is ~30% of the total ash mass, which is much higher than the fraction of submicron ash from coal combustion.

Cofiring of crop residues with coal in existing power plants has been proposed as an

Table 4. Typical coal fly ash properties.

	Typical Value	Range	Notes
Specific Gravity (single particle)	2.2	1.8–2.6	<1 for cenospheres
Specific Gravity (bulk ash)		1.1–1.5	includes voids between particles
Elemental Composition	**Typical %**	**Range %**	**Expressed as Oxides**
Al_2O_3	25	13–36	
SiO_2	45	22–61	
Fe_2O_3	20	4–20	
CaO	2.6	1–22	
MgO	1.3	1–5	
TiO_2	1.2	1–3	
Na_2O	0	0–8	
K_2O	2.1	0.3–4	
SO_3	2	0–25	
Trace Metals		ppm levels	
Phase Distribution	**Typical %**	**Range %**	
Unburned Carbon	3	0 to >10	
Amorphous Glass		50–90	
Crystalline Minerals		11–48	
Major Minerals		**Range %**	
Mullite		2–20	$Al_6Si_2O_{13}$
Quartz			SiO_2
Iron Spinel			$(Mg,Fe)(Fe,Al)_2O_4$
Hematite			Fe_2O_3
Anhydrite			$CaSO_4$

Notes: Typical fly ash composition is for Pittsburgh No. 8 high volatile bituminous coal fly ash; ranges compiled from various sources.[129,187,188]

economical way to reduce PM emissions from open burning in the fields and to replace fossil fuel.[202] Laboratory studies of inorganic species behavior during cofiring have been conducted.[203] A field study of cofiring coal and straw reported a number concentration of 5×10^7 particles/cm^3.[204] This high number concentration may be due to the use of an injector diluter installed directly in the flue.

Domestic Combustion

A significant amount of combustion takes place indoors, for example, tobacco smoking, natural gas appliances, oil-fired furnaces, fireplaces, and wood stoves. Domestic combustion is especially important when considering population exposure to combustion particles on a global basis. Smoke from small-scale domestic combustion of biomass, locally produced coal, and other opportunity fuels results in a direct exposure to sensitive individuals, such as the elderly and children, since the fires are located in or near homes. Fresh and aged wood smoke may be especially important for health effects because the small particle size results in enhanced deposition in the lower respiratory tract.[205] Cooking and heating with biomass represents a large portion of the total combustion in developing economies. For example, household biomass combustion in Pakistan is estimated to represent 37% of the total primary energy consumption of the country.[206]

Poorly ventilated cooking fires can create indoor particle levels that are far above the U.S. ambient PM standard of 150 μg/m^3. A geometric mean kitchen PM$_{10}$ concentration of 1830 μg/m^3 was reported in a study of Bolivian highland villages.[207] The kitchen PM$_{2.5}$ concentration in homes using biomass for cooking averaged 555 μg/m^3 with a maximum of 1493 μg/m^3 (n = 7 homes) in rural Mexico.[208] Recreational biomass fires are a surprisingly large source of combustion emissions in developed countries, and fireplace restrictions have been imposed in many cities and mountain resort communities to avoid violations of the current PM$_{10}$ standard. For example, combustion of wood in residential fireplaces has been estimated to contribute 14% of the annual average OC emissions to the Los Angeles urban atmosphere.[209]

Particle emissions from biomass vary with both the combustion conditions and the fuel type. One study of PM emissions from residential wood fires distinguished between hot, rapid combustion and slower, low-temperature, air-starved combustion.[210] Hot burning produced a monomodal particle distribution with 30–40% of the particles between 0.3 and 0.6 μm. The particles were predominantly EC and OC, but contained percent levels of K, Cl, and S with 0.01–1% levels of Al, Si, P, Zn, Pb, and Fe. For cool burning, the particles were largely OC, and almost 50% of the carbon was associated with particles between 0.6 and 1.2 μm.

Combustion efficiency, wood moisture, and dilution gas temperature affect the particle size distribution, indicating that the actual winter fireplace PM may have a higher fraction of fine particles than are measured under laboratory conditions.[211] Hildemann provided detailed particle size distribution graphs of fireplace emissions and calculated an emission factor of 10 g PM/kg wood burned based on electrical aerosol analyzer size measurements, and reported 16 g/kg based on filter weight.[155] Rogge reported fine particle emissions from fireplaces ranging from 6.2 g/kg for oak to 13.0 ± 4.0 g/kg for softwood,[209] and suggested that unique organic species, such as tricyclic resin acids, can serve as markers of wood smoke in the atmosphere. The amounts of various PAH compounds resulting from domestic combustion of biomass fuels have been reported.[209,212,213]

Regional differences in domestic combustion may provide the opportunity to conduct long-term exposure health studies that integrate epidemiologic methods with detailed characterization of the PM. For example, domestic combustion of coal has been associated with the high incidence of lung cancer in Xuan Wei, China.[214] Chemical characterization of indoor air in homes using smoky and smokeless coals showed 1–2 orders of magnitude differences in the concentration of PAH. The PAH and polar extracts from the particles in homes using smoky coal were highly mutagenic.[215–217]

Wildfire and Agricultural Burning

Open fires from wildland and agricultural burning are a significant source of atmospheric PM on a global scale. Concerns include acute health effects to people near the fires, climate effects,[218] and regional visibility.[219] PM from large fires can be transported over continental distances. High PM_{10} in the eastern United States during the summer of 1998 was caused by smoke from fires in Mexico,[220] as shown by satellite photos. EPA policy[221] does not consider exceedances of National Ambient Air Quality Standards (NAAQS) from natural events such as seismic and volcanic activity, wildland fires, and high wind to constitute a violation for the legal purpose of designating non-attainment areas. However, high particle concentrations are a health and environmental concern whether the source is classified as natural or anthropogenic. Fire is important for recycling nutrients and for preventing the spread of invasive species in many ecosystems. Balancing the ecological role of fire with the goal of minimizing particulate levels in populated areas is a concern for land management in the western United States and in other areas with grassland ecosystems.

Emissions from wildland and agricultural fires are poorly characterized because of the variability in combustion conditions, for example, upwind versus downwind propagation, fuel loading per area, and fuel moisture. Hot fires produce more NO_x, but less CO, unburned hydrocarbons, and soot than smoldering fires. Quantitative data on particle size, number concentration, and chemical composition that would be useful for epidemiology correlations and for mechanistic toxicology studies are limited by the difficulty of field measurements and the uncertainty of how to scale from laboratory experiments to real open fires. Inventory estimates of PM emissions from open fires are based on empirical factors for PM per weight of fuel burned multiplied by an ecosystem-based estimate of fuel loading per area. Typical emissions factors are: 4 g of total suspended PM/kg of biomass burned for piled logging slash with no soil debris; 16 g/kg for smoldering combustion of conifers in temperate forests;[153] and 20 g/kg for tropical forest fires.[222] Emissions of PAH have been measured in a wind tunnel for simulated open burning of cereal grasses and tree prunings.[223,224] Weakly spreading fires were observed to produce higher levels of the heavier PAH with more of the PAH partitioned to the particulate phase. PAH emissions were more strongly influenced by the burning conditions than by the type of fuel.

Oil Pool Fires

Management of large oil spills presents another case of balancing ecosystem health and ambient air quality standards for PM. Igniting an offshore oil spill can reduce the impact on aquatic and shoreline species, but also creates a large plume of particulate air pollution. An understanding of the characteristics of the PM emissions, as well as an understanding of the atmospheric dispersion and clearance, are needed to assess when to burn. Limited data on pool fire emissions are available from laboratory and mesoscale measurements.[225] The PM mass emissions range from 5% of fuel burned (50 g/kg) for laboratory fires to 15% of the fuel for a 17.2 m pool fire, showing that the smoke yield increases with increasing fire size. The particle size distribution from one mesoscale measurement was 50% of the mass in particles less than 0.7 μm and 90% in those less than 20 μm.[226] This is much larger than typical soot emissions, suggesting that the high particle loading in pool fire plumes allows large aggregates to form. The size of the primary particles that form the smoke aggregates increases with increasing fire diameter.[98,227] The primary particle size trends and morphology determined by thermophoretic sampling[228] for TEM examination are consistent with formation of soot on the fuel-rich side of the flame and agglomeration upon local flame interface extinction. Oil pool fire smoke is greater than 90% EC, and the PAH emissions from oil pool fires on water have been measured.[229]

Incineration Emissions

Much research has been done on metal transformations during hazardous waste incineration due to the controversial nature of the projects, and due to regulations that require quantifying metal emissions of incinerators during the permit application process prior to facility construction. Although incineration is a small source of PM emissions on a global scale, the unusual compositions of the waste feeds provide valuable insights into the thermochemistry of trace metals. For incinerators, the ash vaporization is affected by both temperature and Cl concentration, since the chlorides of many metals have a high vapor pressure.[59,230] The formation of submicron particles and the formation of a bimodal particle size distribution in incinerators is very similar to the process that has been observed for coal. Unusual waste streams may result in incineration fly ash containing high levels of volatile metals, but in many cases the bulk of the particle mass from incinerator combustion is the refractory oxides.

An extensive review has been conducted by Linak and Wendt,[59] and Lighty and Veranth[231] have also discussed the issue. The partitioning of a metal in a hazardous waste incinerator depends not only on the temperature[59] and the gas environment, but also on the constituents within the solid matrix.[232] The metals either react with the solid matrix to form solid materials that might be nonleachable, or they may vaporize and undergo nucleation and particle growth similar to the processes previously discussed for submicron inorganic ash from coal. Vaporization also depends upon the type of metal. Normally, Cd[233] is found to be more volatile than Cr; however, the results depend on the solid matrix. The high levels of Cl present in incineration gas-phase emissions compared with fossil-fuel combustion affect the formation of fine PM.[230,234,235] The metal chlorides are generally more volatile than the metal oxides, so Cl causes higher vaporization, which leads to increased formation of submicron particles enriched in trace elements. Differences have been observed between the effect on particle size of inorganic versus organic Cl, that is, NaCl and PVC in the feed,[236] suggesting the importance of intermediate species in the reaction pathway.

If a listed toxic metal remains with the solid, the ash must meet land-disposal regulations, which require a leachability test. Research has shown that Pb may interact with the aluminosilicates in solid materials.[59,237,238] Others have studied the injection of sorbents for metals control, which captures the volatile metals in a sorbent-derived particle.[102,232,239,240] In some cases, a non-leachable solid was formed.

Laboratory-scale elemental composition and particle size data have been reported for conditions applicable to commercial incinerators.[241] Metal speciation data is more difficult to find since the metals are normally present only in trace amounts, which are difficult to detect by many speciation methods. However, Linak et al. demonstrated that the toxic form of chromium, Cr VI, was only a few percent of the total chrome emitted from a laboratory scale system,[242] except in the presence of Cl. When large amounts of Cl were present, the percent emitted was between 5 and 8%, still low. Thermodynamic calculations also show that input waste composition has a greater effect on Cr VI formation than does operating temperature.[243]

Data on full-scale incinerators are collected at the stack to demonstrate compliance with emissions limits. Due to the high particle removal efficiency, the emissions from incinerators are controlled by gas cleaning equipment performance. Combustion conditions impact emissions indirectly through changes in the particle size distribution, which influences air pollution control equipment performance. A study to characterize the performance of various incinerator gas cleaning systems showed that the PM mass concentration, corrected to 7% oxygen, measured at the secondary combustion chamber exit was 5 ± 0.6 mg/m^3, while the concentration downstream of a baghouse and ionizing wet scrubber combination was 0.013 ± 0.009 mg/m^3.[244] The control efficiency for individual elements ranged from 95 to 99.995% removal between the gas cleaning inlet and the stack. The differences in removal efficiency between elements are expected to reflect differences in the partitioning of each element to different particle size fractions, and to the liquid and gas phases. Kauppinen and Pakkanen presented graphs showing the elemental distribution in the emissions from a hospital incinerator,[245] which shows that Pb and Cd are enriched in the submicron particles. The authors are unaware of similar published data on the detailed size distribution of combustion exhaust or stack PM from commercial hazardous waste incineration.

Internal Combustion Engines

IC engines represent 20–40% of the fossil energy combustion in developed countries, and contribute emissions that are concentrated in urban areas. Particulate emissions from engines have been extensively studied due to concerns over the smoke emitted by diesel engines, lead emissions prior to the phase-out of leaded gasoline, and health effects of ultrafine particles. The general process of particle formation as discussed in the fundamentals section is fully applicable to IC engines. However, understanding particle formation in the cylinder of a high-speed engine involves both the chemical kinetics which have been determined from experiments in idealized laboratory flames and the transient temperature and volume changes, fuel/air mixing, and heat transfer unique to in-cylinder conditions.

A large body of specialized literature on IC engines exists. Details of engine design,[246,247] combustion in the cylinder,[248–252] in-cylinder measurements,[253] the use of fuel formulation and additives for soot control,[254] PM from catalytic converters,[255] and the development of particle traps for diesel engines[256] are outside the scope of this paper, and the reader is referred to the cited reviews and collected papers.

The filterable particles from IC engines, including both soot and inorganic PM, are either individual submicron particles or are loosely bound aggregates formed from ultrafine primary particles, as discussed in the fundamentals section. Soot and organic PM result from incomplete combustion. The inorganic particles are derived from fuel and lubricant additives, fuel contamination, engine wear, and ambient PM that passed through the air filter. Caution is needed when looking for data on the fraction of ambient PM attributed to IC engines, because non-combustion particles from resuspended road dust and from the wear of tires and brakes are listed under "mobile sources" in some emissions inventories.

Soot formation in IC engines has been studied due to regulation of the black smoke that can be emitted by diesel engines under heavy load, and due to the importance of soot on radiant heat transfer and flame structure. The topic of soot from internal combustion is covered in detail in books by Heywood[257] and Sher.[258] Empirical data show that diesel smoke emissions increase with load, but can be reduced by improved fuel-air mixing and by better control of fuel injection. Work by John Dec and colleagues[259] using laser sheet visualization has shown that, under typical diesel conditions, the initial premix phase of diesel combustion occurs in a fuel-rich vapor-fuel/air mixture (equivalence ratio of ~4) in the leading portion of the fuel jet, just downstream of the maximum liquid-fuel penetration. This vapor-fuel/air mixture is fairly uniform with a sharp well-defined boundary at the jet periphery.

The measurements show that as autoignition occurs, the fuel breaks down over the whole premixed, fuel-rich region almost simultaneously (i.e., within ~70 μsec), followed very quickly (less than 70 μsec) by PAH formation throughout this region. Then, ~140 μsec later, initial soot formation occurs with very small particles forming throughout large sections of this leading portion of the jet. Within an additional 70 μsec, the entire region is filled with small soot particles whose volume fraction is increasing rapidly. The actual emission from the cylinder to the exhaust manifold is the result of competition between soot formation and soot oxidation. Soot oxidation is reduced when the combustion process is prematurely quenched. This occurs when excessive injection of fuel results in the burning mixture contacting the cylinder walls.

Table 5 summarizes exhaust measurements of particle size and number concentration data from selected studies of diesel and gasoline engines.[27,260–266] The exhaust tailpipe data show that IC engines are a source of particles smaller than 100 nm at initial concentrations greater than 10^6/cm^3, which is consistent with measurements of ambient particle size distributions at various distances from urban highways.[267,268]

The sizes of diesel particulate emission can be approximated by a bimodal lognormal distribution.[262] The nanoparticles in the ultrafine transient mode of diesel engines represent only 0.1–1.5% of particle volume (mass) but 35–97% of the particle number.[262] Most of the PM mass is in a mode with a diameter between 0.01 and 0.1 μm. From the available studies, the relative importance of surface growth and coalescence in determining the particle size in this larger mode is unclear. Typical exhaust PM mass concentrations from well-maintained modern diesel engines are 15–30 mg/m^3.[262] With older engines, the PM mass is higher, the number of ultrafines is much lower, and a condensation or accumulation mode dominates the number distribution.[269] The high particle number of 1×10^9/cm^3 reported for a 1991 Cummins engine by Bagley et al.[260] has led to the speculation that the reduced particle mass emissions in the newer diesels has resulted in increased particle number. The hypothesis is that there are insufficient soot particles to provide surface for the condensation of the heavier organic or acid molecules, which therefore become supersaturated in the vapor phase and nucleate as the exhaust cools in the sampling train.[27]

Gasoline engines have much lower PM mass emissions than diesel engines. Tailpipe particle emission mass is as low as 0.1 mg/mi, and the baseline number concentration is 10^5–10^6 particles/cm^3,[264,266] which is consistent with the reported accumulation mode particle size. Graskow et al.[264] reported that the particle number from gasoline engines is highly unstable and that they observed intermittent spikes in particle number up to 2 orders of magnitude above the baseline. The formation of deposits in gasoline engines, which can contribute to particulate emission spikes, has been reviewed by Kalghatgi.[270] Fuel parameters have a strong effect on the fuel/air ratio at which the maximum gasoline engine particulate emissions occur.[271]

A single instrument cannot measure the entire range of inhalable particles from less than 10 nm to over 10 μm that are potentially emitted by an IC engine. By using both a scanning mobility particle sizer (SMPS) and an aerodynamic particle sizer, the full particle size distribution from an engine can be reported in segments. For a diesel engine, Morawska et al. reported 10^4–10^5/cm^3 in the accumulation mode centered on 0.1 μm and ~1 particle/cm^3 in the range from 1 to 10 μm.[263] One particle at 5-μm diameter weighs the same as 1.2×10^5 particles at 0.1-μm diameter. The uncertainty introduced by interconverting particle mass concentration and particle number concentration data for the purpose of testing health effects hypotheses related to vehicle emissions is apparent.

Mass and surface area of submicron particles are inferred from number and diameter measurements assuming a spherical shape and an appropriate density. Comparisons of filter samples and the total emission mass calculated from integrating particle size and number data agree semiquantitatively,[265] generally within a factor of 2. This difference may not be significant compared with the wide range of PM emissions from real vehicles depending on age, operating conditions, and maintenance history.

Table 5. Selected measurements of particle emissions from internal combustion engines.

DIESEL **Engine & Condition**	**Number Mean**	**Results**	**Reference**
1991 Cummins–various modes with and without catalyst	Nuclei 11–17 nm Accumulation 55–73 nm	>10E9 particles/cm^3. High number count in smallest size bin measured. Size distribution graphs and lognormal fit.	260
Newer catalyst-equipped, LNG-fueled, and older leaded-fuel vehicles	Count Median Diameter 39–60 nm	Exhaust number concentration, 1.5E4 for catalyst, 8.4E4 for LNG, 7.9E5 for leaded.	261
1995 direct injection–various modes	Nuclei 5–9 nm Accumulation 29–40 nm	1–7E7 particles/cm^3. High number count in smallest size bin measured. Size distribution graphs and lognormal fit. Mass 15–30 mg/m^3.	262
Various in-service engines 1983–1996	Accumulation 30–160 nm Also data on 0.3–30 μm size range.	0.7–3.9E7 particles/cm^3 in SMPS range. Particle number increased with increasing power.	263
Review paper	Nuclei 5–50 nm Accumulation 0.1–0.3 μm.	1E7–1E8 particles/cm^3. Graphs of particle number and size vs fuel/air ratio for various engines.	27

GASOLINE **Engine & Condition**	**Number Mean**	**Results**	**Gasoline**
1993 4-cylinder	Nuclei <10 nm Accumulation 70 nm	Emissions highly unstable. Baseline 1E5/cm^3 with spikes to 1E7/cm^3.	264
Review paper	40–70 nm	1E5–1E6 particles/cm^3. Varies with fuel/air ratio.	27
Various automobiles 1994–1997	30–70 nm	Did comparisons of total particle number and filter collected mass over test cycle.	265
Various automobiles 1995–1998	25–107 nm	Compared various results from test cycles. Mass 0.1–9.6 mg/mi.	266

A program of dynamometer tests on 23 in-service spark ignition vehicles ranging from 1976 to 1990 model years showed particulate emissions ranging from 7.2 to 1342 mg/mi,[272] and the OC ranged from 35 to 95% of the total carbon.

Various investigators have reported the chemical composition of IC engine PM as a function of particle size and operating conditions. The PM is a mixture of EC, organic compounds, metal oxides, and sulfates. The exhaust from a typical heavy-duty diesel is 31–41% EC or soot, 25–40% unburned oil, 7% unburned fuel, up to 14% SO_4^{2-} and H_2O, depending on fuel sulfur content, and 13% ash and other inorganic, and there is usually some mass listed under unknown origin.[27,273]

Data on partitioning between soot and the soluble organic fraction[274] and between EC and OC by thermal/optical reflectance from IC engine emissions are available.[272] Detailed organic composition of emissions from in-service gasoline and diesel engines by GC/MS analysis of extracts have also been reported.[272,275,276] As will be discussed in the measurements section, the H_2SO_4 and heavy organic products of incomplete combustion may form particles in the atmosphere that are not included in the PM as measured by standard procedures. In the United States, particulate emissions are regulated by the mass collected on a filter at 325 K (125 °F) followed by equilibration at 295 K and 45% relative humidity before weighing.[277] Figure 13 shows the complex nature of the condensable organic aerosol collected from diesel engines using a dilution sampler.[276] Only a small fraction of particle-bound material is resolved into known compounds, and even the resolved fraction contains multiple chemical compounds within each category. Dilution samplers[155,278] can quantify the mass and composition of the condensable

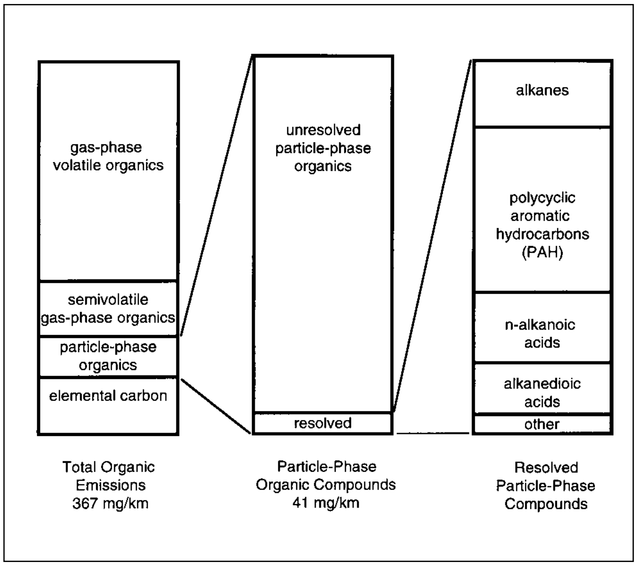
gas-phase volatile organics
semivolatile gas-phase organics
particle-phase organics
elemental carbon
unresolved particle-phase organics
resolved
alkanes
polycyclic aromatic hydrocarbons (PAH)
n-alkanoic acids
alkanedioic acids
other
Total Organic Emissions 367 mg/km
Particle-Phase Organic Compounds 41 mg/km
Resolved Particle-Phase Compounds

Figure 13. Organic analysis of the exhaust emissions from medium-duty diesel trucks. Only a small fraction of the particle-phase organics were resolved into identified compounds. Replotted from data by ref 276.

PM, but may distort the size distribution. The effects of dilution on PM size distribution will be discussed in the measurements section.

Vehicles need to be considered as a potential source of particle-bound transition metals in health-related studies. Table 6 provides illustrative data showing the metals content of diesel and gasoline emissions, and shows that IC engine emissions have significant metal content. Metals are reported in mg/mi for the average of two in-service diesel trucks sampled in 1996 in California[276] and for the average of four 1995 model-year Ford automobiles.[279] The variation in the data is large, and only the elements where Schauer et al.[276] reported a mean greater than twice the standard deviation are listed. The total mass emissions from the gasoline contain 9–31% metallic elements by weight. PM emissions of 27 elements from in-use high-emitting vehicles were reported by Cadle et al.[280]

Table 6. Metals emissions from internal combustion engines.

	Diesel Trucks	Automobiles
Total Mass	845 ± 22	7 ± 4
EC	260 ± 9	NR
OC	166 ± 6	NR
Si	5.3 ± 0.2	0.12 ± 0.12
Fe	0.42 ± 0.02	0.11 ± 0.09
Zn	0.59 ± 0.03	0.009 ± 0.005
S	1.86 ± 0.07	0.7 ± 0.9
SO_4^{2-}	8.5 ± 0.5	NR
NH_4^+	6.2 ± 0.3	NR

Notes: Emissions in mg/mi were calculated by the authors from data reported by Schauer et al.[276] and Ball.[279] NR = not reported.

Leaded gasoline has been phased out in the United States and in many developed countries, but it is still used. The particulate emissions from automobiles burning fuel with 0.4 g Pb/liter are about 25% Pb,[281] and the mass mean particle size is 1–2 μm,[248] which is much larger than the PM from spark ignition engines running on unleaded fuel. The Pb emissions are on the order of 60 mg/mi. The measured Pb concentration also reflects dilution by the higher EC and OC content of emissions from gasoline engines that are not equipped with modern pollution control technology. Use of methylcyclopentadienyl manganese tricarbonyl (MMT) as an octane-boosting additive results in the emission of amorphous manganese sulfate and phosphate particles with a size ranging from 0.2 to 10 μm.[282]

Modern IC engines produce PM in both the ultrafine mode and in a larger accumulation mode, with nearly all the mass being in particles smaller than 1 μm. Emissions of PM, unburned hydrocarbons, NO_x, and CO all have declined as stricter regulations on new vehicle models have forced improvements in combustion technology and in post-combustion gas cleanup. The limits of current technology are being reached, and air-quality models are predicting an increase in total emissions from vehicles in the next decade as increases in vehicle-miles driven begin to outweigh the reductions in emissions that have been achieved by retiring older vehicles. Health concerns regarding particle number, ultrafines, and transition metals will lead to a need for more detailed characterization of IC engine emissions, especially under in-service conditions.

Aircraft Turbines

The aircraft PM emissions literature includes studies addressing both ground-level emissions near airports[283,284] and cruise altitude studies emphasizing stratospheric chemistry and global climate effects.[285–288] Visible smoke emissions from aircraft engines were first regulated by the 1970 Clean Air Act. The engine manufactures retrofitted jet aircraft with smokeless combustors by 1978,[289] and there is little published research on soot emissions from gas turbines from the late 1970s until the mid-1990s. Ground-level PM measurements show that most of the particle mass is soot and semivolatile products of incomplete combustion. Cruise altitude particle number is dominated by H_2SO_4 aerosol. Table 7 compares the mass, size, and number concentration for ground-level testing of engines representing 1970s[290] and 1990s[285] design technology. Conversion to smokeless combustion chamber designs has reduced particle mass and number concentration. However, aircraft engines still can be a locally significant source of submicron particles.

Table 7. Ground-level emissions from aircraft turbine engines.

	Stockham, 1979		Petzold, 1998[a]	
Engine Type	TF–30, JT8D, JT9D		Rolls Royce	
Particulate Mass	Idle	1.85–4.41g/kgfuel	Total carbon	
	Cruise	0.29–2.09	0.27–0.74 g/kg fuel	
	Takeoff	2.8–7.06		
Particle Size	Idle	0.043 μm	Primary	0.045 μm
	Cruise	0.69	Coagulation	0.18
	Takeoff	0.60	Coarse	0.56
Particle Number Concentration	Idle	9.3×10^7/cm^3	Primary	8×10^5/cm^3
	Cruise	2.27×10^7	Coagulation	2.5×10^4/cm^3
	Takeoff	1.9×10^7	Coarse	1.5×10^3/cm^3

[a] Particle number reported by Petzold was measured 200 m behind the engine and was not corrected for dilution.

EMISSIONS, AMBIENT CONCENTRATION, AND INHALATION EXPOSURE

The legal authority of air quality agencies extends only to the component of exposure that is attributable to ambient air,[291] and indoor air quality is controlled indirectly through public health advice, building codes, and product design regulations. Most of the average person's day is spent indoors or in vehicles, and sensitive individuals, infants, the sick, and the elderly spend even more time indoors than healthy working adults. Indoor particle concentrations can be very different from the outdoor ambient particle concentration that is measured by central monitoring stations. The indoor PM concentration and size distribution depend on the rate of outside air exchange, personal activity patterns, and indoor particle sources. In general, the concentration of coarse particles is lower indoors than outside, but activities such as sweeping, or even walking on a dusty carpet, can resuspend large quantities of coarse PM.

Institutional buildings have central air-handling systems that include filtration. A comparison of air samples in patient areas of three hospitals showed little correlation between indoor air PM_{10} and ambient PM_{10} at local air monitoring stations.[292] A better correlation is observed between indoor and outdoor fine-particle concentration. Accumulation mode ambient PM can penetrate into buildings because these particles are not efficiently removed by gravitational and inertial mechanisms. However, activities such as cooking and tobacco smoking are indoor PM sources that can increase fine-particle concentrations far above ambient levels. Personal exposure to particles depends on physical activity (ventilation rate) and on the amount of time spent in various environments indoors, in vehicles, and outdoors.

Health effects research must look at the actual human exposure, and many of the indoor sources involve combustion-generated particles. When discussing the health effects of combustion particles, one must consider that, with the exceptions of domestic combustion and tobacco smoking, people do not directly inhale combustion emissions. Persons inhale particles that have undergone post-combustion and atmospheric transformation. Different particle sizes are removed from the atmosphere at different rates, and the particles may become coated with condensable species. The cells deep in the lung are not exposed to the same particle mixture that is measured by an ambient filter, due to size-selective removal in the airway. Some gas-phase chemicals that would ordinarily be removed by diffusion to the airway wall may penetrate deep into the lung when adsorbed on an inert particle, the "Trojan Horse" hypothesis.

Ambient PM Characteristics

As originally reported by Whitby and Sverdrup,[293] and since confirmed by many studies, atmospheric particles have a multimodal size distribution, as shown in Figure 14.[6,293–296] These modes include the coarse mode, which is usually mechanically generated; the accumulation mode of 0.1–1 μm particles; and a mode of fine particles resulting from nucleation and surface growth. The latter two modes are the consequence of nucleation, condensation, and coagulation to produce particles from gas-phase precursors. The true accumulation mode is the result of particles growing into the range where further growth is slow, because of decreased collision frequency, and where removal is slow, because inertial deposition and gravity settling are inefficient. The size and shape of the ultrafine particle mode in the urban atmosphere represents a dynamic balance between the generation of new particles (nuclei) by nearby sources and growth into the accumulation mode by coagulation and surface deposition.

The process of forming new particles by nucleation and the subsequent growth by coagulation and condensation are similar both in combustion systems and in the atmosphere. Nanoparticles are created from vaporized compounds by gas-to-particle conversion due to chemical reaction or cooling. These reactions may take place in the combustor, during initial dilution of the plume, or over a period of hours in the atmosphere. Nanoparticles are rapidly removed from the atmosphere by coagulation

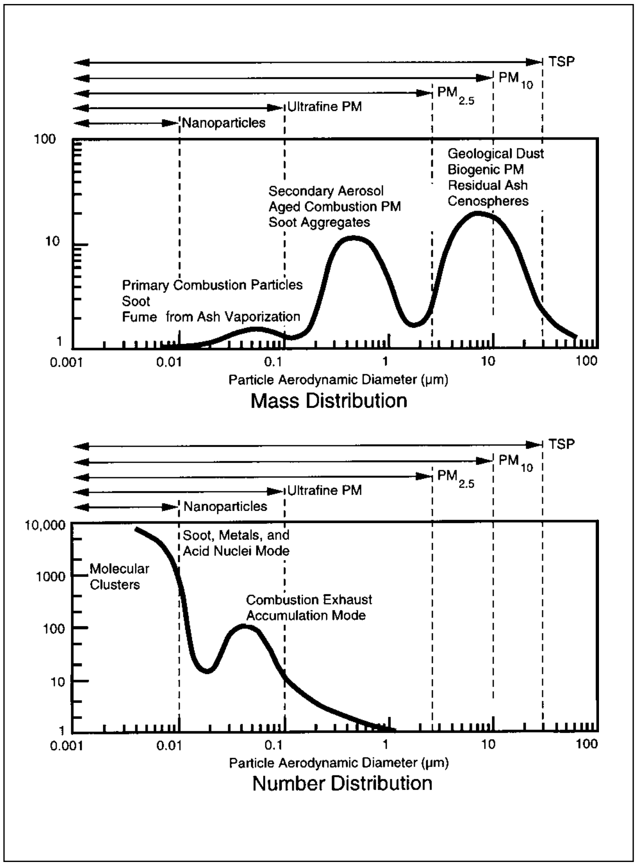

Figure 14. Typical PM mass and number distributions showing the multimodal nature of the ambient aerosol. Adapted from data by refs 6 and 293–295.

with each other and with larger particles. In addition, species condensing from the gas phase are deposited on ultrafine particles since they represent a large fraction of the available surface area. These condensing species include organic compounds, SO_4^{2-}, and NO_3^- formed by reactions in the atmosphere from precursors that are emitted as gases from combustion systems. Eventually, the ultrafine nuclei-mode mass is transferred into the accumulation mode consisting of particles between 0.1- and 1-µm diameter. Accurately measuring the ultrafine size distribution, in both the ambient air and combustion source emissions, is difficult because particle number is not conserved, ultrafine particles undergo rapid transformations, and there are few calibration standards available. Seinfeld and Pandis provide a detailed treatment of ambient aerosol characteristics.[6]

Gravimetric measurements of particle mass generally show only the coarse and accumulation modes unless the data are plotted on a logarithmic scale. Likewise, optical and electrical mobility measurements of particle number usually show only the nucleation and accumulation modes. Natural PM includes wind-transported geological material, biogenic PM (pollen, spores, and secondary PM from VOCs), and sea salt. Naturally released sulfur and nitrogen compounds produce additional PM, but the anthropogenic emissions of sulfur and nitrogen compounds dominate secondary particle formation in industrialized areas. Comparison of oceanic, polar, and remote desert aerosols[297] to urban aerosols[293] shows that the natural nucleation and accumulation modes are small compared to the anthropogenic contribution to fine PM. Reported concentrations of ultrafines in ambient air vary from 100 to 1000/cm^3 in rural and oceanic environments, 10^4/cm^3 time-averaged in urban areas,[298] and ~10^6/cm^3 near an urban freeway.[6] Janecke[297] provides quantitative descriptions of typical ambient aerosols as the sum of three log-normal distributions, which are useful for modeling input.

Source Apportionment and Modeling

Figure 15 shows that 80–90% of the PM mass emitted from combustion sources is below 1-µm diameter, while less than 10% of the mass of dust from geological material is $PM_{2.5}$.[294] However, the evidence for the relative contribution of various $PM_{2.5}$ sources is contradictory, and some source apportionment studies[299] suggest that ambient $PM_{2.5}$ is dominated by sources other than combustion particles. For example, Figure 16 shows ~62% of emissions coming from geological material and only 38% coming from combustion sources.[300,301] Emissions inventories are based on multiplying census-type data by emission

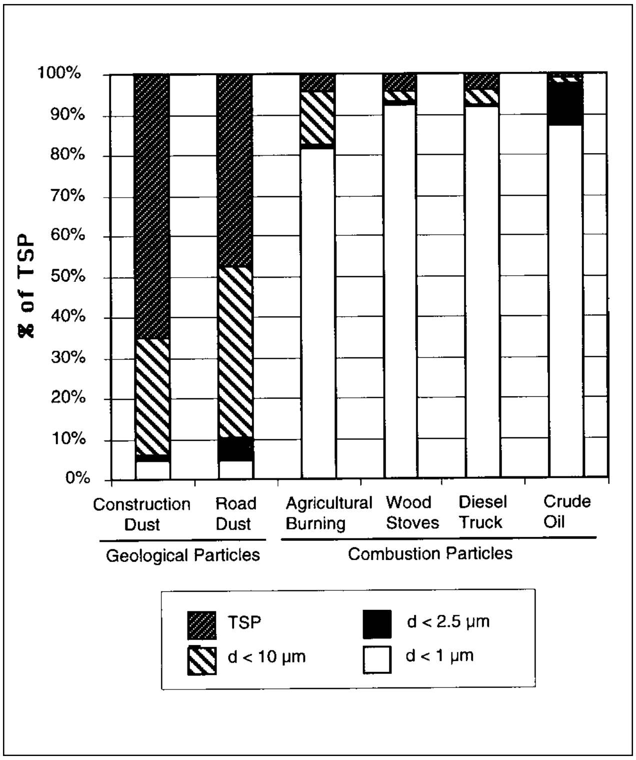

Figure 15. Typical size distribution for the emissions from geological dust sources and from combustion sources. PM_1 dominates the mass of combustion emissions, while most geological dust is larger than PM_{10}. Replotted from data in Watson and Chow.[294]

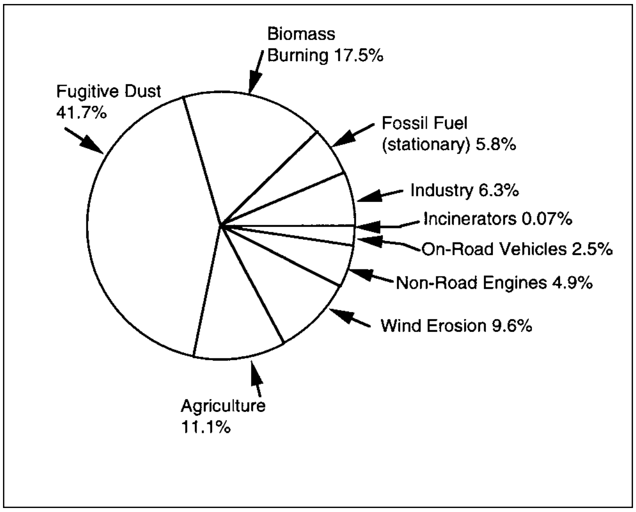

Figure 16. Inventory of the 1997 U.S. nationwide $PM_{2.5}$ emissions.[300] Total mass was estimated as 10 Tg/yr. Major differences exist between inventory data and source apportionments based on the composition of particles collected at receptor sites. Source: U.S. Environmental Protection Agency.

factors, which are often based on only a few measurements. Both researchers and air quality agencies suspect that the fugitive dust component is overstated by these methods.[294] If the fugitive dust is overstated, then some other contribution, such as combustion, is understated, as many urban areas are in violation of the PM standards. Suspected sources of the differences between emissions inventory and receptor-based methods of calculating source contributions include comparing national averages which are dominated by rural areas with monitoring stations which are concentrated in urban areas; not fully accounting for redeposition of wind-blown PM near the source area; and not including the effect of "super-emitter" sources such as improperly maintained and operated combustion sources in the inventory emission factors.

As EPA compiles information from speciated PM monitoring sites, it will be interesting to learn more about the chemical characteristics of ambient PM and how this can relate to specific sources, including combustion. International variation in the relative contribution of combustion and geological processes to ambient PM are expected because of local climate, geography, and technology preferences. For example, in urban areas in Taiwan, $PM_{2.5}$ was found to be as high as 80–90% of PM_{10},[302] and combustion was found to be a major source of both the coarse and fine PM.[303] Likewise, particles larger than 2.5 μm, or even larger than 0.5 μm, are rare in the central European urban environment.[304]

The combination of particle size and chemical composition data provides insights into the sources. For example, the $PM_{2.5}$ in the eastern United States has a much larger SO_4^{2-} component and a much smaller NO_3^- component than does the $PM_{2.5}$ from California.[305] This result is likely due to the effects of coal-fired power plants in the east and of agriculture and mobile sources in the west. Source apportionment based on matching chemical composition of particles collected from known sources with the mixture collected at receptor sites is an active area of research.[294,306–308] Reconciling source inventories with the particles actually collected at receptor sites has important public policy implications.

A mechanistic air quality model has been developed that allows computing the contribution of individual emission source types to the size and chemical-composition aerosol distributions.[309] The model predicts that the submicron fraction of the PM does not contain appreciable amounts of secondary particles. Specifically, little SO_4^{2-} and no NO_3^- was predicted in the particles less than 0.1 μm. For particles between 0.1 and 1 μm, SO_4^{2-} concentration was slightly higher with a larger increase in NO_3^- concentration. Data from filters confirmed the modeling results,[310] although the sulfur concentration in the particles less than 0.1 μm was higher on the filters than predicted. The model explains the measured 0.2- to 0.3-μm particles as transformed emissions from diesel engines and other combustion, and explains the observed 0.7- to 0.8-μm particles as fine background aerosol that has been transformed by fog and gas-to-particle conversion in the urban air.[310] The model predictions are only as accurate as the source data and the atmospheric transformation chemistry models.

The observed particle size distribution in urban environments is the result of a dynamic balance between generation of ultrafine particles by combustion sources and the transfer of these particles to the accumulation mode by coagulation and by surface growth from secondary aerosol gas to particle conversion. While computational modeling may provide insights into the relationships between sources and human exposure, models are limited by the source data, and there is a need for more detailed characterization of combustion sources.

PARTICLE HEALTH EFFECT RESEARCH

Particles have long been implicated in the deterioration of visibility and the environment and as the cause of adverse health effects. As early as 1661, John Evelyn wrote,[311] "It is this horrid smoake, which obscures our churches and makes our palaces look old, which fouls our clothes and corrupts the waters so that the very rain and refreshing dews which fall in the several seasons precipitate this impure vapour, which with its black and tenacious quality, spots and contaminates whatever is exposed to it." Evelyn goes on to say, "London fires, there results a great quantity of volatile Salts, which being sharp and dissipated